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CARLSBAD CAVERNS AND OTHER CAVES OF THE GUADALUPE BLOCK, NEW MEXICO[1]

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ABSTRACT

The limestone caves of this region were made under completely saturated conditions long before the present erosion cycle began and probably before the Pliocene Ogallala formation was deposited.

INTRODUCTION

In the combination of four unusual characteristics the group of caves in the Guadalupe Range of New Mexico appears to be unique. It contains one of the deepest known caves of phreatic origin (Carlsbad), it possesses caves with gypsum flowstone, it exhibits carbonate flowstone outcrops and stalactitic debris in the mantle rock above caves, and it yields evidence of former fillings of green —not red—clay. As in other cavernous regions described by the writer (Bretz, 1938, 1942), the caves of this group are older than the topography. They are older than the great Capitan reef scarp in which and behind which they occur, older than the broad Pecos lowland east of the scarp, older than the latest uplift of the Guadalupe block, and probably older than the peneplain across the summit of the block.

Two of the seven caves studied in detail are partly or wholly in the Capitan reef rock, four are in the nearly flat-lying rock of the rugged summit country west of the scarp, and one is in the flank of a minor anticlinal fold well down the northern slope of the block. There are fifteen to twenty other caves in the region, some difficult and time-consuming to reach and all reported to be minor affairs.

The Guadalupe Mountain block (fig. 1) is triangular in ground plan and is tilted up along its southwestern margin. From an indefinite northern margin, possessing broad lowlands of 3,500–4,500 feet A.T. among its hills, in the latitude of Carlsbad, the general surface rises between two southward-converging lines of cliffs to culminate in about 35 miles as a great prow of 8,751 feet A.T., 4,000 feet above a salt flat to the southwest and some 3,000 feet above the country to the southeast. The western cliffs are largely fault-determined. The eastern scarp is commonly described as essentially the seaward slope of a great Permian reef, now standing in relief because of erosional removal of weaker sediments to the southeast.

The tilted triangular upland itself is

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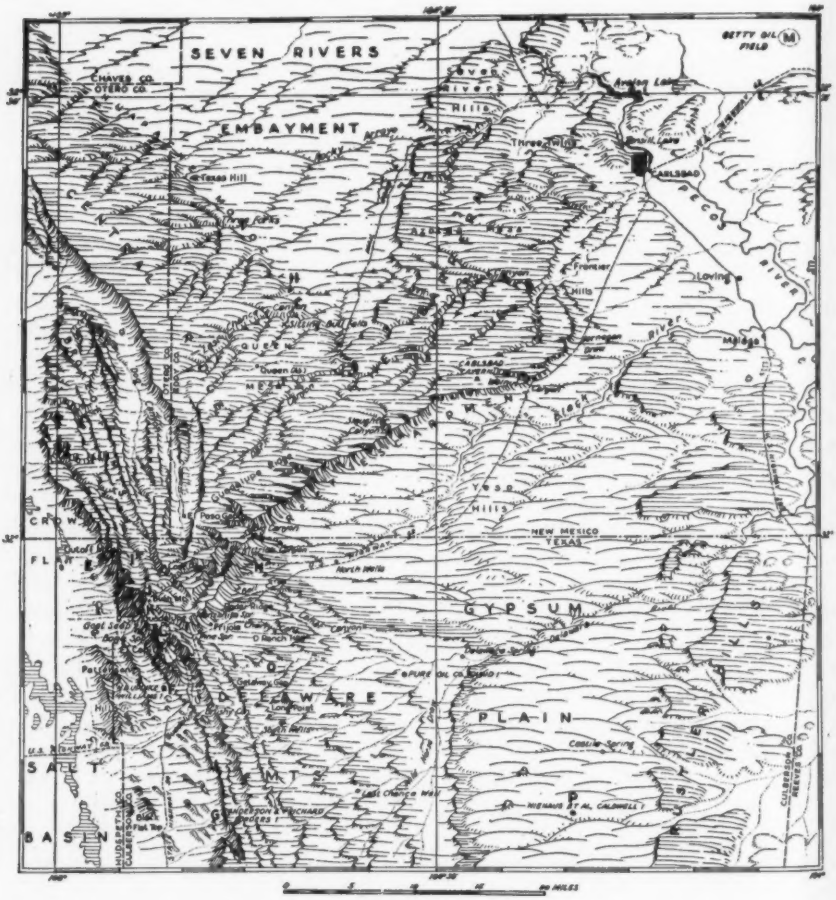
somewhat warped and faulted, and a considerable part of the western side is dropped in a series of narrow faulted slices known as the "Brokeoff Mountains," lying parallel with the main western cliff. Almost no drainage leaves the Guadalupe upland for this much-faulted country and the enclosed salt basin beyond. Most streams flow eastward or northeastward and escape by way of the block's lowest corner, where the reef pitches underground and its scarp disappears. There they enter the Pecos lowland.

A limestone gravel-covered plain at the foot of the reef scarp extends northeastward from the Texas–New Mexico line, becoming a part of the Pecos lowland nearer Carlsbad, where the gradually lowering scarp disappears. Close to the foot of the scarp the plain consists of imperfect alluvial fans, but most of it is a series of terraces dissected by Black River and its tributaries from the moun-


SEVEN RIVERS
EMBAYMENT
GYPSUM
PLAIN
DELAWARE
SALT
BASIN
NEW MEXICO
TEXAS
CARLSBAD
Texas Hill
Three Rivers
Loving
Frontier Hills
Yeso Hills
Queen Hills
Grayburg Hills
Seven Rivers Hills
Artesia
Lovington
Hobbs
Jal
Eunice
Monument
Maljamar
Orla
Malaga
Whites City
Carlsbad Caverns
Guadalupe Mts.
Last Chance Mts.
Brokeoff Mts.
Pecos River
Black River
Delaware River
Dark Canyon
Cottonwood Creek
Rocky Arroyo
Lake Arrowhead
Cooper Spring
Cottonwood Spring
Double Lakes
Red Lake
Salt Lake
Laguna Grande de la Sal
Bottomless Lakes
Carlsbad Reservoir
Carlsbad Caverns Reservation
Hackberry Draw
Dog Canyon
Last Chance Canyon
Rattlesnake Canyon
Slaughter Canyon
Walnut Canyon
Lechuguilla Desert
Hackberry Lake
Pierce Canyon
Pierce Canyon Draw
Loving Draw
Laguna Plata
Laguna Toston
Laguna Tinaja
Laguna Sabinal
Laguna Grande
Laguna Chiltipin
Laguna Gatuna
Laguna Tule
Laguna Salada
Laguna Tomasita
Laguna Patricia
Laguna Mosquito
Laguna Tonuco
Laguna Piedra
Laguna Toro
Laguna Redonda
Laguna Grande de la Sal

tains and interrupted by collapse sinks. Black River low-water discharge vanishes under and reappears from beneath this fill several times in a stretch of a few miles. The subsidences and subterranean river courses are doubtless due to solution in underlying Permian fore-reef evaporites, chiefly gypsum.

In few places have geologists found more intertonguing and lensing and lateral intergrading of stratigraphic units than in the Guadalupe Mountains and the Pecos lowland and Delaware Mountains to the southeast and east. Most of the caves, however, are in the Capitan reef rock or its intertonguing back-reef correlative, the Carlsbad limestone. Their entrances are high in the spurs or walls of ravines cut by Pecos tributaries crossing the reef front. Carlsbad, by far the largest and deepest, is entered from almost the very brink of the scarp summit.

CARLSBAD CAVERNS

The known vertical range in this cave, from the ponor entrance on the ridge top to the surface of an unsounded pool in the lowest chamber, is 1,025 feet.[2] The entrance (4,350 feet A.T.) is 300 feet above the bottom of Walnut Canyon, 3,000 feet distant to the north, and about 550 feet above the base of the scarp, 3,500 feet away in the opposite direction. Thus the cave, extending down to 3,325 feet A.T., is an air-filled cavity, 725 feet below the bottom of Walnut Canyon and 475 feet below the upper limit of the gravel deposit at the foot of the scarp. This gravel plain, descending about 150 feet in the first mile away from the scarp and more gently with increasing distance, finally reaches the altitude of the cave bottom, 10 miles or more from the scarp.

[2] Revision of figures supplied by the National Park Service and published by the author in 1942.

The location of Carlsbad Caverns, more than 1,000 feet deep in a ridge $1\frac{1}{4}$ miles wide at the base and 400–600 feet high[3] (fig. 2), definitely disposes of the idea that the cave is a product of ground-water work during the present cycle of erosion. The cave system is older than the scarp. There is good evidence that the system once extended up into rock now eroded from the ridge summit and scarp face. The evidence is found in Chimney Cave and some associated topographic sags on the upper slopes of the scarp near Carlsbad's entrance. Chimney Cave is simply an unroofed vertical slot, reported to be 150 feet deep but to show no marked horizontal expansion. The opening is about 125 feet lower than that of Carlsbad and is on the top of one of the minor ridges between the short ravines scarifying the scarp face. The ridge east of Chimney Cave has a shallow ponor on its western slope, and, farther along the line between Chimney and the ponor, the crest of this ridge is made up of huge blocks of reef rock, lying at all angles, out of harmony with the otherwise uniform reef-bedding but displaced only by subsidence, not by having gravitated down along the slope. Still farther east along this line and across another ravine is a second shallow ponor, margined by big tilted blocks. Two or three other sunken tracts, 100–200 feet across, lie near by, likewise with displaced blocks that dip radially inward and also with flowstone fragments and a flowstone-cemented breccia in place (see pl. 1, *A*). Two good specimens of broken stalactites were found in these sags. One of the sags is reported to lie directly above the Jumping Off Place of the cavern.

Further evidence that Carlsbad was

[3] The ponor entrance is 100 feet below the ridge summit.

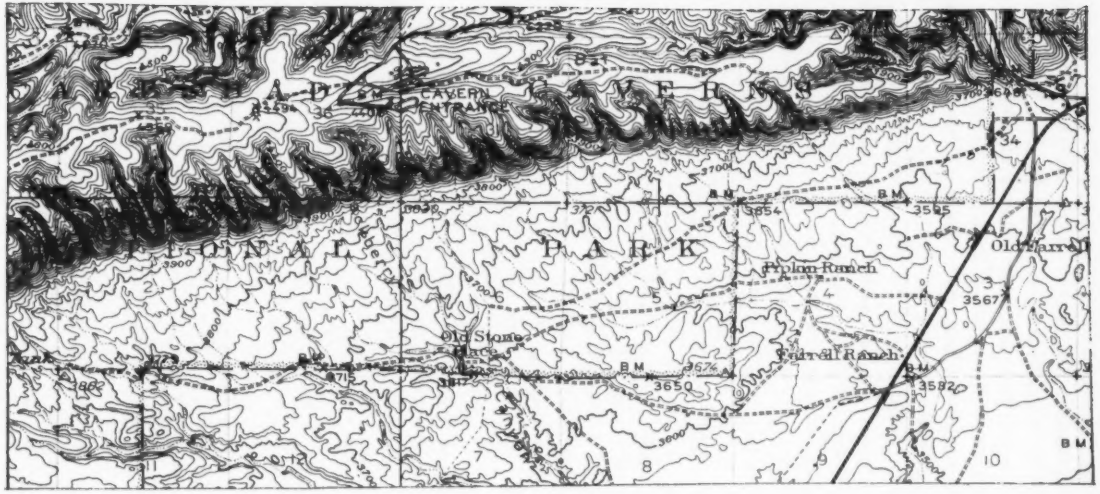


FIG. 2.—Map of environs of Carlsbad Caverns. From Carlsbad Caverns East topographic map, U.S. Geological Survey

made below a higher land surface than the present ridge summit is encountered immediately on entering the cave. The ponor collapse is asymmetrical, an uncollapsed part of cave wall and ceiling now being exposed to daylight. Tubes and pockets of solutional origin exist in the walls not more than 30–50 feet below the ground surface. They belong to that large category of minor cavities in cave walls and ceilings which record differentially greater local yielding to solution rather than locally greater vigor of attack on uniformly soluble rock (Bretz, 1942). Spongework belongs to the same category, and Carlsbad's magnificent display of spongework is to be seen from the highest to the lowest levels of the cave. Only below the water table can such solutional yielding occur on all bounding surfaces of a cave.

The argument for phreatic origin of Carlsbad also includes the joint-controlled network well shown by the cave map (fig. 3). Solutional enlargement and extensive collapse have so modified some chambers that, from inspection alone, one hardly recognizes the original joint control. But the great system has all gradations from narrow vertical slots to the Big Room, almost all elongated north-south or east-west, in conformity to the joint system. Particularly instructive is the Left Hand Tunnel, a narrow route to a great hole, the lowest place in the cave. The Tunnel is a tight, vertical slot quite unsuited for tourist inspection. In places its controlling joint is multiple, and the passage becomes four closely spaced slots with partial or complete partitions. The spongework of the Tunnel is unsurpassed in any cave that the writer has ever seen.

In three separate places Carlsbad possesses a record of vadose stream water whose flow was subsequent to the phreatic making of the cavern. One of them is a continuous stream channel, at least 1,500 feet long, in the Lower Chambers. It is situated so far down in the system that, if the former cave stream emerged at the foot of the scarp, there could have been no gravel fill within 200 feet of the altitude of the one now banked against that scarp.

An alternative to this suggestion is that an unknown subterranean route, miles in length, carried its water to the Pecos Valley. The river now is about 25 miles distant and 500 feet lower. The cave stream's gradient, by aneroid, was nearly 90 feet per mile. This must have been decreased to 20 feet per mile for this suggested long underground course, unless the valley was considerably deeper than it is today. Perhaps the extensive solution in evaporites of the Permian White Horse, Castile, Saludo, and Rustler deposits underlying the Pecos Valley provided opportunity for wholly subterranean discharge well over into Texas. It is difficult to dispose of the indicated volume and presumed load by infiltration through the gravel of the foreland, and a deep stage of Pecos drainage, either surface or subterranean, seems required.

This free-surface stream followed the floor of such phreatic passages as provided gradient for its needs. Direction of flow, recorded by gradient and by imbrication of cobbles, was south, then west, then *north*, away from the scarp! Obviously, it was not determined by a water-table slope and was not escaping very successfully from under the reef scarp. It found the floor of the chambers that it used already covered with silt, and it cut a channel in the silt from 3 to 4 feet deep at the accessible upstream end and from 16 to 18 feet deep at the lower accessible end. Gravel bars indicate a flood depth of 6 feet. The stream did not

operate very long, for it failed to modify the limestone walls with the horizontal undercuts and meander niches that many vadose cave streams have made and are making on phreatic chamber walls.

Another vadose stream record exists off the northeast corner of the Lunch Room Chamber. The passage is low, with limestone gravel and later flowstone too near the ceiling to allow a traverse adequate for determining gradient. The cobbles, fairly well worn and ranging in diameter up to 16 and 18 inches, are im-

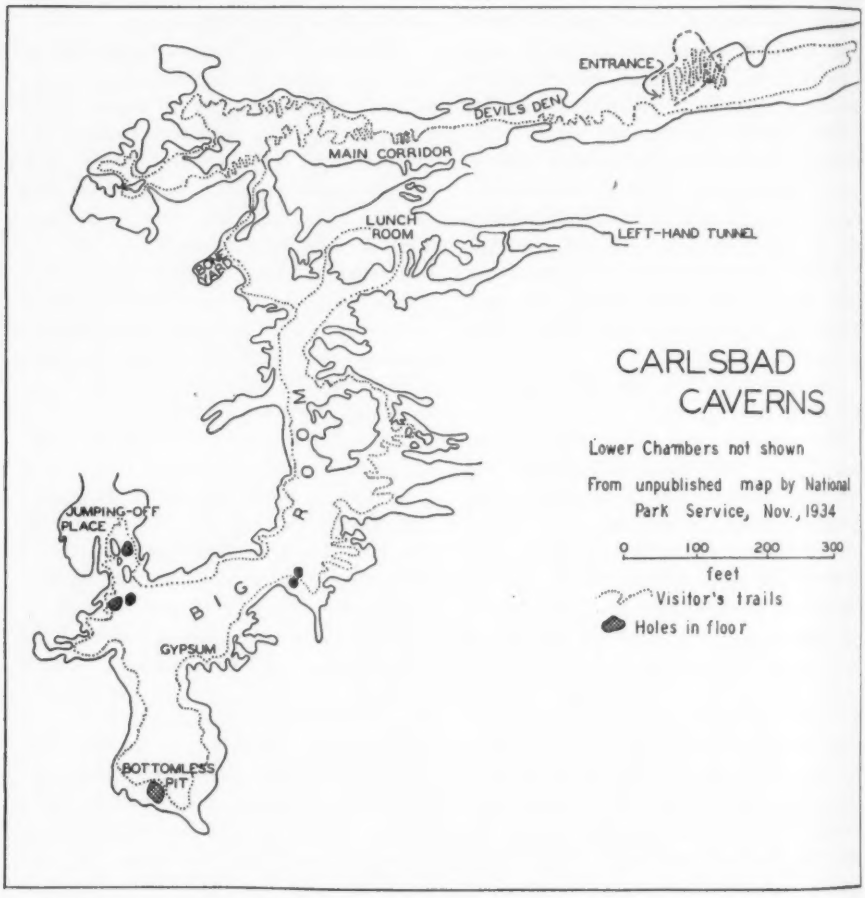


FIG. 3.—Map of main part of Carlsbad Caverns. After National Park Service unpublished map

PLATE 1

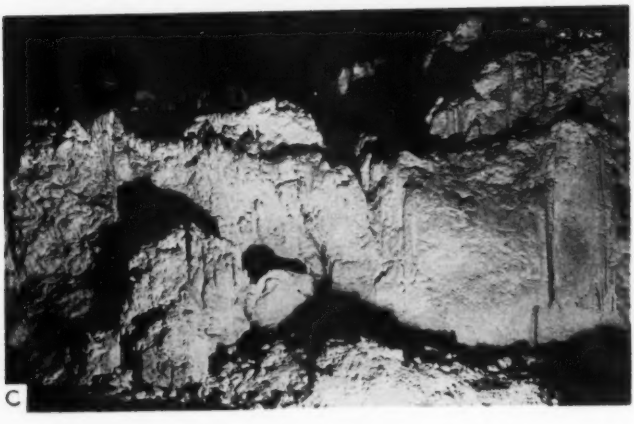
A, Blocked cave opening on slope of reef scarp near Chimney Cave. L. Horberg, photo.
B, Flowstone from valley slope near entrance to Hidden Cave.

B

Specimen of flowstone

A

Blocked cave opening



Carlsbad Caverns features

bricated to show that the stream entered the much larger chamber from the north. Obviously, the Lunch Room Chamber (it seats 1,000 people) was already in existence when the vadose stream took origin.

The original floor of the Lunch Room had some deep slots or holes, now filled and covered with concrete.[4] Probably this vadose stream plunged down such a hole, to become, 90 feet lower, the stream of the Lower Chambers. Fallen rock and dripstone deposits prevent following the deeper portion upstream to the foot of the postulated fall.

Apparently this segmented stream of two portions succeeded an earlier and smaller vadose stream along the same routes, the record being the silt terraces (pl. 2, *A*) along both routes and also at the entrance to the Left Hand Tunnel from the Lunch Room. The deposit is well-sorted, laminated fine sand and silt, with no intercalated pebble layers. The terraces constitute flat-topped and accordant remnants, now separated because of the channeling of the cobble-carrying successor and, in the Left Hand Tunnel entrance, because of slump-pit development there. The change from a small, silt-depositing stream to a large, cobble-transporting one came abruptly. The earlier stream may well have been born of seepage water from the ridge above, but the later discharge can best be explained as an underground detour of some surface stream, which, in down-cutting, discovered a part of the deep phreatic system and utilized it for a time. This is no improbable procedure; for other caves are known where surface streams, having done this very thing in the past, later returned to their surface valleys and deepened them well below any possible future reuse of the cave route. Walnut Canyon bottom, ½ mile or so distant, is still 300–400 feet higher than the Lunch Room floor and probably was yet higher at the time that the cave stream functioned. Although, in flash flood, it is a considerably larger stream than the underground channel could care for, the suggested explanation can be adapted by detouring only part of the stream because of a constricted entrance route.

Stalagmites, coming to light as silt slumps down at the Left Hand Tunnel entrance, prove that the first vadose stream did not begin functioning for some time after the cave was drained.

A third deposit of stream gravel, apparently unrelated to the two already discussed, is near the top of the descent to Devils Den. It consists of limestone pebble gravel and fills phreatic wall pockets of a narrow, channel-like passageway lateral to the great main corridor. A few pebbles of green clay in the deposit were derived from near-by remnants of that clay in other pockets.

[4] "Beneath the center of the Big Room floor is a maze of phreatic passage ways at a level intermediate between the Big Room and the Lower Cave. This consists of a network of fairly long tubes at right angles to each other and contains beautiful spongework. The presence of this intricate system along the two major joint zones gives further evidence that the Big Room was once a network of phreatic passage ways arranged both horizontally and vertically, and that continued solution and collapse have opened it into the present huge chamber" (Bennett Gale, personal communication).

PLATE 2

A, Silt terrace and cobble-covered channel floor, Lower Chambers, Carlsbad Caverns. B. Gale, photo.
B, Reef bedding in Capitan limestone, Bottomless Pit, Carlsbad Caverns. B. Gale, photo.
C, Drip solution holes in cave gypsum deposit, Big Room, Carlsbad Caverns. B. Gale, photo.

Green clay has been found in Mystery Room, in the Lower Chambers, and in several places in the Big Room. Its vertical range is almost as great as that of the cave. In both Mystery Room and the Big Room it has become oxidized or stained to a red or chocolate color on the surface and along laminations and desiccation cracks. Excavations for trail-making materials in the Big Room show no intercalated coarse material or secondary lime deposits. It may, therefore, be a phreatic clay deposit, made when the Guadalupe region was a peneplain, when differential hydrostatic pressures and circulations had disappeared because of the destruction of the prepeneplain relief.

There are, however, three arguments against this view: (1) In the Big Room, where much ceiling rock has fallen, some clay lies largely unburied, hence must postdate most of the collapse and should therefore be late vadose in age; (2) the ridge tops, even the broader, flatter summits, carry only a thin, interrupted soil mantle, and there is almost no clay in it; (3) the capacity of Carlsbad is so enormous that one hesitates to consider that the cavern has ever been clay-filled and then re-excavated, as have caves with similar phreatic-vadose history under humid climates. Further study may show that the clay in Carlsbad records more than one episode.

Remnants of an apparently once continuous deposit of white, massive, unstratified gypsum lie on the floor of the Big Room and in marginal chambers of the Lunch Room. The maximum exposed thickness is about 20 feet. It is younger than some carbonate flowstone, but great stalagmites sit on top of it and therefore are still younger. It seems that the gypsum can only be the consequence of local pooling during the vadose history, recording temporary conditions when sulfate alone was precipitated. A local source may have been the Permian gypsum both outcropping and known in wells close to the base of the near-by scarp and higher than these cave-chamber floors. Dripping water in many places has later dissolved vertical tubes in this gypsum (pl. 2, *C*). Some big blocks of the gypsum have lost 50 per cent of their bulk by such drilling. One hole is 12 feet long and only 3–4 inches in diameter. Elsewhere, carbonate flowstone and stalagmites have covered the gypsum.

NEW CAVE

About 9 miles along the scarp southwest from Carlsbad Caverns, the mouth of Slaughter Canyon constitutes a notch 1,300 feet deep in the reef front and a mile wide at the top (fig. 4). Two caves have been transected by this notch, one on each side. Each cave is about halfway up the canyon wall. The close proximity of the small Midnight Canyon, southwest of Slaughter Canyon notch, has made a sharp spur in the scarp front, and a saddle in the spur isolates a summit hill at the tip, less than 30 acres in area. New Cave lies under this hill, scarcely more than 150 feet below the level of the saddle.

Entrance to New involves descent of a long cave talus deposit whose debris has come from the canyon slope. The fan has spread a convex foot out into three subparallel chambers and has mounted up around the separating pillars or walls. The debris is composed of thin, flat slabs, dipping into the cave with the talus slope but obviously not derived from the local Capitan reef rock. It is Carlsbad waste and either came down from higher surfaces or was introduced by the stream when the canyon was only half as deep as now.

Two other transections of the cave system lie east of the enterable opening and at the same level. One may be traversed for about 50 feet to a jumping-off place, beyond which the spotlight shows considerable continuation. This cliffy slope with the three cave-chamber cross sections also possesses much slabby, cemented talus, the dip of the slabs being toward the wall, away from the canyon. Clearly, there were other old cave chambers here, now completely blocked with waste from the outside.

The total vertical range of New Cave is but little more than 100 feet. Most of the chambers are high and relatively narrow openings along three sets of joints, approximately north-south, north 40° east, and east-west. One group of six such chambers, varying in heights and lengths but all close-set and connected, possesses the potentiality of becoming one large chamber under sufficiently long-continued phreatic conditions.

The horizontal extent southward must bring the cave very close to the opposite

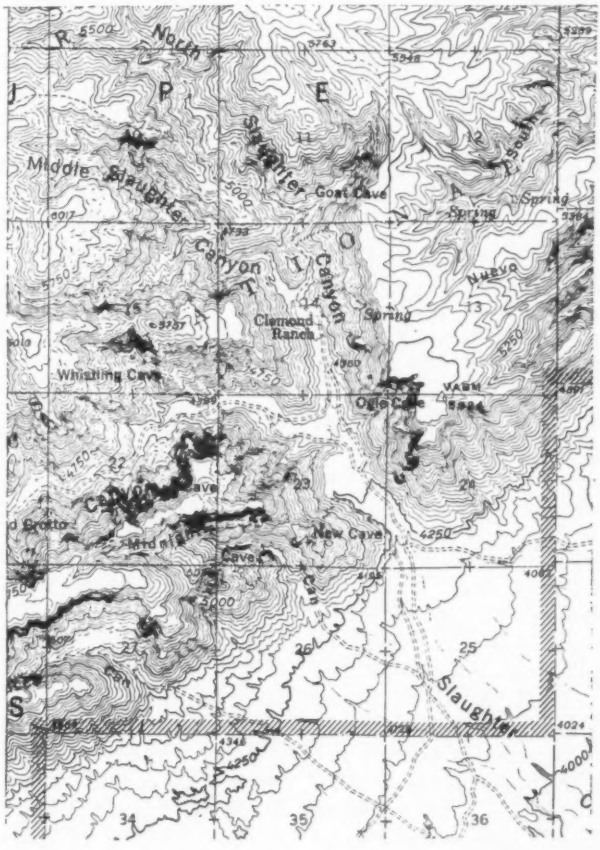


FIG. 4.—Map of Slaughter Canyon and environs. From Carlsbad Caverns West topographic map, U.S. Geological Survey.

side of the hill on the spur tip, under which New Cave lies. This idea is supported by the heavy flowstone deposits, which, sloping northward, block the cave at the south end.

No evidence of vadose water-work, other than the secondary deposits, was seen in New Cave. Although the canyon stream has cut away part of the cave, it apparently never found an underground traverse possible. The joint control of high, narrow, slotlike chambers, the bridgings across those slots, the windowed partitions, the ceiling and wall pockets, and the abundant spongework are as positive affirmations of phreatic origin as the cave's situation, high under the 30-acre tip of a spur carved from the reef scarp, is positive denial of vadose origin. New Cave, like Carlsbad, is older than the lowland east of the Capitan escarpment.

A feature of New Cave's dripstone, unique in the writer's experience, is solutional spongework or near-spongework in some of the stalagmites. Resolution of stalagmites by drip water is not rare, but this spongework has been made, as has cave-wall spongework, under conditions of complete submergence. The best display is in the giant stalagmites near the entrance. They are old and dull and have suffered wastage mostly by the penetration of large irregular cavities on all sides. These cavities transect the concentric growth structure, producing a striking similarity to the grain of a block of carved wood. The outstanding exhibit is a compound stalagmite, 15 feet or so in diameter and 20 feet high. Differential solution has largely spared the top while eating away the sides, so that the form produced suggests a gigantic canopy umbrella or toadstool, the underside of the cap and the irregular stem showing the grain noted above. A few subordinate lower shelves or partial canopies are comparable to the cap. Later dripstone here and in many other places has covered some of these corrosional outlines. Unpocketed stalagmites must have grown later or have had such ravages entirely hidden by renewed growth.

Was this solutional submergence, after a vadose experience, an isolated affair in New Cave because of local and temporary conditions? Does it record a return to phreatic conditions along the whole scarp? Evidence presented later in this paper seems to make the second alternative as satisfactory a choice as the first.

Another interesting feature of New Cave's dripstone is that some of it is gypsum-coated and that some selenite crystals are $\frac{1}{2}$ inch in diameter. The Christmas Tree stalagmite is a great compound form, with a snow-white coating of gypsum in which sparkle the larger crystal faces. No dripstone composed wholly of gypsum and no gypsum flowstone were seen in the cave.

COTTONWOOD CAVE

This cave is situated high in a divide, the Guadalupe Ridge (see fig. 1), which lies parallel with the scarp for 15 miles or so and some 4 miles back of it on the dissected oldland. The ridge presumably is an imperfectly reduced portion of the uplifted peneplain recognized in the summit uplands of the mountain block. The cave mouth is only 100 feet below, and $\frac{3}{8}$ mile distant from the ridge crest at Dark Lookout, 6,850 A.T.

Cottonwood Cave is a simple linear chamber which extends for $\frac{1}{4}$ mile back under a minor spur among Black River headwater canyons. The detrital floor descends 225 feet in that distance, and its ceiling descends 150–200 feet. The controlling joint strikes north 15° west

and in places shows in the ceiling as a solutionally widened slot with some surviving bridgings. The mouth of the cave is 500 feet above the canyon floor, $\frac{1}{8}$ mile distant.

The overlying ridge is so narrow that, if Cottonwood's orientation were 90° to its length instead of about 45°, the cave would completely perforate the ridge. With no other evidence of the character of the cave, the conclusion is inescapable that it antedates the canyoning. Surviving bridges high in the ceiling slot are positive evidence of its phreatic origin. The descent of the cave back into the ridge and under surfaces 100 feet higher than at the mouth is impossible for ground water, phreatic or vadose, to have made during the present cycle of erosion. Indeed, the cave comes so close to the trace of the peneplain that we seem almost required to date its phreatic origin as earlier in that erosion cycle.

Uncommon features of caves, but well shown in Cottonwood, are slicing and falling of nearly vertical slabs parallel to the wall. The partings by which future slices will become disengaged dip very steeply back into the walls on either side. Were the cave developed deep beneath a former land surface, these diverging cracks might be the record of incipient failure by shearing under heavily loaded roof rock.

Cottonwood has two groups of huge dripstone growths, one within reach of sunlight, the other about 300 feet farther back. Descent over some 50 feet of in-sloping talus leads to the first and much more massive group. The thickness of the roof rock over this place is about 30 feet, and the volume of the secondary calcite deposits is so great that, if they have grown by contributions only from the existing roof, it should show evidences of this great loss. Yet the ground surface, 30 feet above, shows no trace of sinks or collapse or a generally carious condition. Nor could this calcium carbonate have been brought laterally from very far, for the ridge is narrow and steeply sloped. It is concluded that these marked accumulations were made before the heads of Black Canyon's two tributaries had reached the locality and, by their deep incision, had left the narrow ridge.

BLACK AND HIDDEN CAVES

Four more caves lie in this high country near Cottonwood, all close to the divide and none more than 2 miles from Dark Lookout. Two small unnamed ones are shown on the Carlsbad Caverns West topographic map under a spur ridge whose flat summit is essentially a peneplain remnant. Black Cave's entrance is 250 feet below this summit, near the bottom of Cave Canyon. The entrance to Hidden Cave is about halfway down the side of another small canyon, 500 feet deep at the cave.

Both caves, transected by ravine growth, have been nearly sealed up because of gravitative migration into them of hillside waste. Each cave has maintained an opening to the outside only because, as ravine widening has pushed the hillside back and shortened the cave, ceiling fracture at intersection with the hill slope has persistently continued and slope retreat has carried the opening higher and higher (fig. 5). To reach the true solutional cave, one descends a sloping chimney bounded on one side by fractured bedrock and on the other by in-sloping talus and flowstone.

Hillside waste below each opening contains fragments of dark-brown, laminated, sublustrous, slightly translucent travertine, identical with the weathered flowstone exposed at the entrances (pl. 1, *B*). One mass down the slope appears

to be in place. Some of this flowstone is cementing material of a breccia. These materials are relics of the two caves' former extensions, now destroyed by later ravine-making. Because the elongation of Hidden is approximately 45° to the strike of its transecting valley slope, the travertine debris is traceable in a long diagonal down the slope. There can be no reasonable doubt that the canyons are later than the caves and that the lime which went into making the flowstone came from vanished roof rock.

of a small pool in which gypsum was deposited. The deposit is now disintegrating into a loose sandy detritus.

The strike of the cave is north 10° west, almost paralleling the ridge crest to the east and the valley bottom to the west. It is difficult to visualize either vadose or phreatic ground water following a course so related to its associated topography unless special conditions demanded. Joint control in a cave so close to a steep hillside seems quite inadequate, and no other cause is indicated.

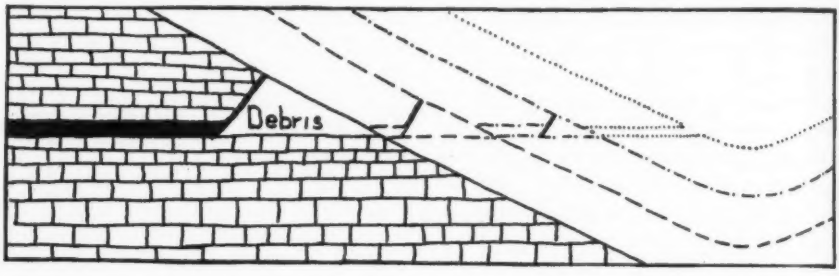


FIG. 5.—Diagram to show up-slope migration of entrance to Hidden Cave as the outside valley was enlarged.

Black Cave's chambers consist of three closely spaced, joint-determined openings, the separating partitions being scarcely thicker than the openings are wide. There is a short connecting cross-chamber. Walls converge upward to make steep-gabled ceilings, which repeatedly show solutional pocketings and groovings along the joint. Dripstone blockades terminate the open passages.

There has been much spalling from walls, some slices still unfallen but free from wall rock. This has destroyed original solutional outlines, has widened the passages from earlier slotlike proportions, and has made a fill of unknown depths.

In the wealth of secondary carbonate deposits in Black Cave, there is a record

Black Cave, therefore, is confidently interpreted as a phreatic solution feature antedating the valley dissection of this plateau-like portion of the Guadalupes. It lies scarcely 250 feet below the peneplain trace.

Hidden Cave's ground plan involves six or seven connected, straight, narrow passages recording three joint sets, which strike north 10° west, north 27°–30° west, and north 80° east. The main north 10° west passage, where entered, is double, the separating partition hanging from the ceiling, its lower part completely dissolved away. The eastern of these two parallel passages terminates in a short distance with the joint showing in the end wall. It is essentially a huge wall pocket. At the south end of the travers-

able cave is a chimney slot which opens to daylight above and leads down 20–30 feet into an apparently east-west passage. Lack of sufficient rope prevented examination of this lower opening.

The imperfectly developed joint-controlled network plan is sufficient evidence that Hidden Cave is of phreatic origin. Vadose conditions arrived, and flowstone deposits were made before Dark Canyon's tributary heads had been extended back into the upland as far as the cave's location. Much of the original cave was later obliterated by valley erosion outside and dripstone deposition inside.

MUDGETT'S CAVE

The mouth of this cave is about halfway up the cliff of Dark Canyon in the last of the dozen or so large entrenched meanders called "Serpentine Bends." It is 300 feet above the stream bed and best reached from the divide between Walnut and Dark canyons. It is readily traversable for at least 750 feet back under the hill, its fairly straight horizontal course lying north 75° east, at right angles to the cliff face. The detrital floor slopes back into the hill, away from the canyon. Although there has been much wall failure, enough spongework remains to testify to a phreatic origin.

Three ravines have nearly isolated the hill above the cave, its small area and steep slopes above cave level being quite inadequate, even during earlier stages of the present erosion cycle, for gathering the ground water that made the cave.

There are two more caves in the vicinity of Mudgett's, each revealed by a chimney perforation at the surface but neither now possessing much horizontal extent underground. The chimneys have no associated sinks and appear to be collapses into chambers below or simple intersections of high slots by the erosional lowering of the surface, and not the products of descending vadose water.

One of the unnamed caves is about a mile south of Mudgett's, close to the bottom of Lechuguilla Canyon's minor dissection of the upland back of the scarp. Its chimney opening is determined by the intersection of two vertical joints. More high slots of the former cave appear to be recorded by two or three nearby outcrops of a dark, coarsely crystalline cave onyx or flowstone, between adjacent walls of Carlsbad limestone. The original laminations still show well, crossing the cleavages of the completely recrystallized material.

McKITTRICK CAVE

The only cave of this study lying well removed from the reef is McKittrick. It is about halfway up the eastern slope of a 250–300-foot hill near the northeastern corner of the Guadalupe block. The hill is on the apex of a definite anticlinal structure, and the cave is in strata dipping 10°–15° northeastward. Although no chamber is more than 20 feet high, the cave's enterable vertical range is all of 100 feet.

McKittrick Cave, early in its development, was a network of linear passages along two sets of joints, one in the strike, north 50° west, the other along the maximum dip. Widening of the intersecting joint slots of the original rectangular pattern has been so great that many of the once separating blocks, pillars, and partitions have been destroyed except near the upper end of the cave. But the ceiling throughout and the surviving attenuated pillars record the earlier joint control. Splendid dome cavities in the ceiling are also products of phreatic solution. Under later vadose conditions, the ceiling joints have determined lines of stalactites and sta-

lagmites. Some partitions have been constructed by the growth of rows of coalesced columns. The cave is an excellent example of an intermediate stage between an early network and a late complete coalescence into a large room.

The only gypsum cave flowstone known to the writer covers a large portion of McKittrick's floor, extending from the highest to the lowest enterable portions and attaining a maximum exposed thickness of 5 feet. It originally had depositional terracings on its surface, the steepened fronts still recognizable. Partial destruction has been largely by later drip water which has drilled innumerable vertical holes in it, identical with those perforating Carlsbad Caverns' gypsum deposit in the Big Room. Partial obliteration has come from the growth of carbonate stalagmites on it. Some stalagmites, however, appear to be older and therefore to penetrate up through the sulfate flowstone.

The source for this gypsum is not the rock of the present hill. The cave is in the Yates limestone, well up toward the top of the Guadalupe series. The Ochoa rocks, stratigraphically about 200 feet higher and once overlying, are gypsiferous; so is the Yates or its correlative strata, about 5 miles to the west.[5] If the gypsum came from Ochoa strata, as seems probable, the cave became vadose while denudation lacked at least 200 feet of producing the present topography.

Like all Guadalupe caves—indeed, like almost all limestone and dolomite caves known to the writer—McKittrick Cave is in its decadence. It is filling with secondary precipitates and with collapse detritus from three collapsed places in its roof. There have been chambers of this cave above the present hillside surface, now completely erased, but with fragments of their flowstone and dripstone still lingering on the slope. Caves are destroyed under vadose conditions, rarely made.

[5] Oral information from Carl Branson.

AGE OF THE CAVES

Every Guadalupe cave examined has yielded what seems to be incontrovertible evidence that it antedates the present erosion cycle and therefore antedates the making of the existing reef scarp and the lowland east of it. Three of the caves are but little below the trace of the former oldland, which now survives only in isolated flattish summits. One cave records a vadose stream whose vigorous current found escape much below the level of the gravel flat abutting against the base of the reef scarp. For this escape, a postpeneplain Pecos Valley deeper than the present one seems required.

In addition to this stage of postpeneplain erosional history, another event in regional history must now be introduced, one that, for weeks of the field work, was difficult for Dr. Horberg and the writer to accept but which accumulating evidence during the work finally forced upon us. It is a depositional item; the existence of quartzose Rocky Mountain stream gravel, not alone in the Pecos lowland, where it had previously been reported (Meinzer, Renick, and Bryan, 1927; Fiedler and Nye, 1933; Morgan, 1938) but also on the summit of the reef scarp. Two significant occurrences will be described and their relation to cave history indicated.

The summit of the scarp between the deep notches cut by Rattlesnake and Slaughter canyons is an elongated, flattish surface descending gradually northeastward for 750 feet in a little less than 4 miles. Correlated with other comparable upland flats, both on the reef top and back of it, the flat appears to be a good record of the tilted peneplain (see fig. 4). Its highest or southwest end is

5,500 feet A.T., nearly 1,500 feet above the upper edge of the piedmont limestone gravel deposit. This mesa-like upland carries many thousands of worn, siliceous stream pebbles and in one place shows an indurated remnant of the old quartzose gravel deposit *in situ*. The deposit occurs in an unroofed, surviving portion of a former cave!

The remnant, accompanied by several acres of scattered loose pebbles, lies at the head of Nuevo Canyon, between 5,425 and 5,475 feet A.T. Quartzite, chert, jasper, and vein quartz are all represented in what is probably the best display of these foreign pebbles seen in either the Guadalupe upland or the Pecos lowland.

Remnants of the cemented deposit range through 50 feet of altitude at the canyon head. The uppermost exposures show brown lime-sand strata associated with granule-gravel strata. Down along the ravined head of Nuevo for 200 feet and through a vertical range of 50 feet, remnants of a pebble conglomerate lie in cracks and cavities of the limestone. Most contacts are nearly vertical. In one is a slight overhang of the limestone wall.

This relationship would be an inadequate basis for the assertion that the quartzose conglomerate is a cave-filling almost on the brink of the 1,500-foot scarp. The former cave, however, is recorded by the largest and best display of weathered, recrystallized, laminated flowstone encountered during this study. Like the river gravel, it is distributed in loose pieces and is also in place, filling cracks and cavities in the limestone. As loose material, it occurs only in the immediate vicinity of flowstone and quartzose conglomerate *in situ*. Minimum dimensions of the former cave or group of solution cavities were about 200 feet horizontally and 50 feet vertically. The flowstone is considered good evidence of a once roofed condition and must be older than the summit flat.

A relationship sought by three pairs of presumably trained eyes was flowstone fragments in the conglomerate or siliceous pebbles in the flowstone or at least a flowstone-conglomerate contact. None was found. There are some large angular pieces of limestone embedded in flowstone, presumably fallen ceiling or wall rock. The conglomerate seems best considered as younger than the flowstone and surely is younger than the solution cavities which it fills. If the mesa top is a peneplain trace, the old cave was made still earlier and was destroyed in the final stages of that erosion cycle.

Further evidence that a scarp existed when the gravel was deposited is found along a poor trail traversing the second shallow draw on the scarp face, north of the mouth of Slaughter Canyon. Almost directly east of, and at least 400 feet below, the 5,524 bench mark on the upland's summit, two vertically elongated, dikelike bodies of indurated siliceous conglomerate crop out in the reef rock along the trail. One of them has much associated flowstone, but no contact of gravel and flowstone was found or fragments of either in the other. Whether or not these were solution slots, there apparently was a scarp face existing here at the time of gravel deposition, and it has retreated so little that pebbles still linger in its reentrant cracks.[6] If the indurated quartzose conglomerate being trenched by Black and Pecos rivers is a lower part of the same deposit recorded on the mesa summit, the scarp was even higher in prequartzose time, and, barring differential movement along the scarp, the

[6] The only alternatives are to consider these as clastic dikes, with associated flowstone, whose pebbles migrated 400 feet down into open joint cracks, or as pebbles caught in these cracks as they slid down the present scarp face.

deposit attained a thickness of at least 3,100 feet.

The quartzose gravel and calcareous sand deposit on the summit is believed to be a western part of the Ogallala formation which, 40 miles to the east, constitutes the Llano Estacado of the Texas Panhandle. If this is correct and if the solution cavities and flowstone about the head of Nuevo Canyon are of the same age as the caves and surface exposures of flowstone elsewhere beneath the summit oldland and also if the Ogallala formation is Pliocene in age throughout, then it follows that the peneplain is either pre-Pliocene or had been made by the time the fill was complete, and that Carlsbad, New, and other caves are products of ground-water work in earlier stages of the peneplain cycle.

Fragmentary bones found in the vadose stream channel northeast of the Lunch Room in Carlsbad have been identified by C. L. Gazin of the United States National Museum as of *Nothrotherium*, a Pleistocene ground sloth. If they were carried into this part of the cave by a detoured surface stream, the channel and the deeper Pecos Valley, to which it must have discharged, are of Pleistocene age. This postulated deep stage of Pecos Valley is not to be confused with the original making of the lowland and the first appearance of the scarp. That original lowland extended on eastward into Texas beneath the great, high-plain Ogallala remnant—the Llano Estacado. The deep stage is a post-Ogallala valley or series of sinks with subterranean drainage, and it marks the reappearance of the scarp. The piedmont limestone gravel is post-deep stage.

A pre-Ogallala scarp must have been canyoned, and Ogallala sediment must have been deposited in such canyons. Relocation of modern canyons on old canyon sites appears to have destroyed the record of this. If it ever is found, the concept here advanced will become unassailable.

If the caves are of prescarp age and if the Ogallala formation later filled the eastern lowland and lapped over onto the reef summit, an early vadose experience of the caves must have been succeeded by a return to phreatic conditions. The spongework of some of New Cave's great stalagmites can be considered a record of this second phreatic experience. Failure to find a similar record in the other caves may mean only that their dripstone is younger or that their spongework in secondary limestone has been entirely covered by additions during the present vadose experience.

What were the conditions under which deposition of calcium carbonate ceased in some of the caves, was succeeded by deposition of calcium sulfate, and that followed by a return of lime deposition and a re-solution of the gypsum? A more fundamental question deals with the precipitation of the sulfate. Obviously, the familiar explanation of escape of CO_2 does not apply. For these questions the writer has no answers.

ACKNOWLEDGMENTS.—Closely associated with the writer in the field work and discussion on which this paper is based was Dr. Leland Horberg, of the University of Chicago. Thanks are gladly given him for suggestions, counsel, and a healthy skepticism until adequate evidence had accumulated. It is pleasant to record the wholehearted co-operation of the administrations of Carlsbad Caverns National Park and Lincoln National Forest during the field study. Particular thanks are due to Park Superintendent Donald Libbey, Park Naturalist Bennett Gale, Park Ranger Tex Worley, and Forest Ranger John McCollum, who volunteered as guides to and through some of the caves. The field expenses of the study were met by a grant from the R. D. Salisbury fund of the University of Chicago.

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GEOMORPHIC HISTORY OF THE CARLSBAD CAVERNS AREA, NEW MEXICO[1]

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ABSTRACT

The upland surface of the Guadalupe Range and three younger erosion surfaces in the Pecos lowland record progressively lowered base levels during the Pliocene and Pleistocene. Structurally, transverse consequent drainage in the range is attributed to superposition from a Pliocene (Ogallala) cover uplifted by block-faulting. Carlsbad and other caverns antedate the present topography and are believed to be related to a pre-Ogallala cycle of erosion.

INTRODUCTION

GENERAL STATEMENT

Carlsbad Caverns National Park in southeastern New Mexico is situated along the southeastern rim of the Guadalupe Range and overlooks the Pecos lowland to the east (fig. 2). The summit peneplain and high-level gravels, in the range, and terraces and valley fill, in the lowland, provide a basis for an interpretation of the main late Cenozoic events in the region. These events can be related to the time of cave development[2] and are of regional interest in their bearing on the genesis of the Pecos depression.

The area studied during 5 weeks of the summer of 1947 includes the central part of the Guadalupe Range and the adjoining Pecos lowland, east to the Pecos River (Carlsbad, West Carlsbad, Carlsbad Cavern West, Carlsbad Cavern East, and Malaga quadrangles of the U.S. Geological Survey) (fig. 3). Numerous traverses, which were made across the Pecos depression between Santa Rosa and the Texas boundary, provided a background of regional relations.

PHYSIOGRAPHIC SETTING

The physiographic boundary between the Pecos section of the Great Plains and the Sacramento section of the Basin and Range Provinces (Fenneman, 1930) follows the Reef escarpment at the southeast margin of the Guadalupe Range and essentially bisects the area studied (fig. 3). The range thus is the easternmost of the Basin ranges and is a fault block tilted to the northeast.[3]

Physiographic studies in the Roswell Basin and adjoining regions north of the area (Meinzer *et al.*, 1927, pp. 6–16; Fiedler and Nye, 1932, pp. 10–18, 25–41, 95–113; Morgan, 1938, pp. 9–17; Morgan and Sayre, 1942, p. 35) resulted in the recognition of five cyclical surfaces (fig. 1), from oldest to youngest: (1) the Sacramento plain, an upland surface west of the Pecos which truncates the structure on the north slope of the Sacramento Range and is correlated with the constructional surface of the High Plains to the east on the Ogallala formation; (2) the Diamond A plain, a subsummit rock plain, 400–1,300 feet below the Sacramento plain, which is correlated with gravel-capped mesas along the western edge of the Roswell Basin and with the Mescalero plain east of the Pecos; (3) the Blackdom terrace, a sloping

[1] Manuscript received April 26, 1949.

[2] See companion paper by J H. Bretz.

[3] For a detailed treatment of the stratigraphy, structure, and geomorphology of the southern Guadalupe Range and adjoining areas see King (1948). This report was not available at the time that the present paper was written.

plain west of the Pecos underlain by limestone gravels and situated 55–90 feet above present drainage; (4) the Orchard Park terrace, a similar plain, 25–40 feet above present drainage; and (5) the Lakewood terrace, which is 20–30 feet above present streams and underlain by silty alluvium. All but the Sacramento plain are considered to be Pleistocene in age.

In the Carlsbad Caverns area it is possible to recognize the three lower terraces, and it is probable that the Guadalupe upland surface is equivalent to the Sacramento plain.

The prominent Reef escarpment is a unique geomorphic feature. It is the exhumed front of a Permian reef. Southwest of Carlsbad Caverns the escarpment is due to massive southeast-dipping reef beds of Capitan limestone; northeast of the caverns it is produced by upper beds of Carlsbad limestone, which cover the reef and dip 10° southeast (King, 1942, p. 639).

The Pecos lowland is underlain by the Castile anhydrite, Salado halite, and Rustler limestone of the Ochoa series, which overlies the Guadalupe beds.

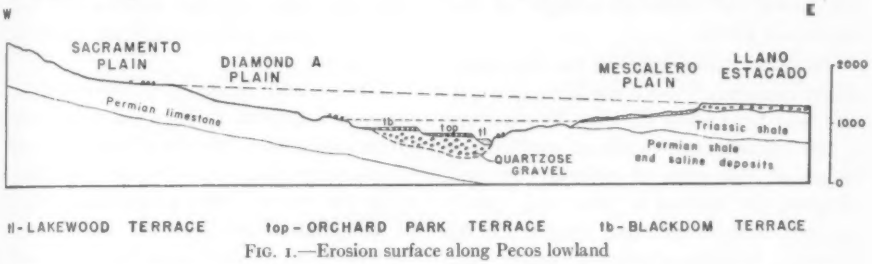


FIG. 1.—Erosion surface along Pecos lowland

GEOLOGICAL RELATIONS

The rocks of the Guadalupe Range are largely limestones belonging to the Permian Guadalupe series, which dip gently to the southeast and northeast. The mountain block consists of two marginal limestone uplands, which converge southward to give it a distinctive triangular shape. The northwest upland prong is underlain by limestones of both the Guadalupe and the underlying Leonard series, and the northeast prong ("La Barrera del Guadalupe" of Lang, 1937, p. 839) is underlain largely by Carlsbad and Capitan limestones of the Guadalupe series. The Carlsbad and Capitan limestones are stratigraphic equivalents and represent, respectively, back-reef and reef facies. Seven Rivers lowland, which separates the two uplands at the north, is eroded in an anhydrite wedge of the Guadalupe series (King, 1942, p. 553 and pl. 1).

DRAINAGE AND CLIMATE

The entire area lies within the Pecos drainage basin and is drained by intermittent streams which enter the lowland from the southwest. The Pecos River and lower Black River are the only permanent streams.

The climate is semiarid, with a mean annual precipitation of 12.71 inches and a mean annual temperature of about 60° F. at Carlsbad. Most of the precipitation falls as showers during the summer months.

SUMMIT PLAIN IN THE GUADALUPE RANGE

DESCRIPTION

Almost the entire summit of the range is marked by accordant ridge crests and flat summit areas which descend to the northeast, truncating more than 3,000 feet of strata. In local areas truncation,

although readily observed, is not a prominent feature (pl. 1, *A*). However, it is strikingly revealed by comparison of generalized contours of the upland with structure contours (fig. 2). Extensive flat summit areas occur on broad divides and on an upland plain covering several square miles in the vicinity of Queen. The reconstructed surface descends from elevations of about 8,000 feet near the southern apex of the range to elevations of about 4,000 feet near Carlsbad Caverns, an average slope of about 130 feet to the mile. This clearly is not an original slope and must be due to later tilting by faulting along the western margin of the mountain block.

The largest remnants of the plain have slight local relief, with shallow open valleys and broad low divides. The surface is cut off abruptly without gradational slopes at the rims of present canyons. Most of the surface is bare rock, thinly covered with weathering debris and alluvium. Solution-enlarged joints and sinkholes occur in many areas.

GRAVELS ON THE SUMMIT PLAIN

Siliceous gravel residuals occur in the upland plain in (1) the vicinity of Carlsbad Caverns; (2) near Jurnigan Draw, 7 miles northeast; and (3) on the uplands northeast and southwest of the mouth of Slaughter Canyon at elevations ranging from 3,750 to 5,950 feet. Pebbles of crystalline schist and foreign chert are reported[4] from Ares Peak, 22 miles west of Carlsbad Caverns at an elevation of 5,782 feet. In addition to these gravel residuals, conglomerate *in situ* is preserved in solution-enlarged joints at three localities near Slaughter Canyon—at the head of Nuevo Canyon, at a point just below the southern tip of the upland north of the mouth of Slaughter Canyon, and at the head of Yucca Canyon,[5] about 3 miles southwest.

More than 50 per cent of the conglomerate is made up of siliceous pebbles, which, in order of abundance, are chert, quartz, quartzite, and jasper. Most of the deposit is a granule gravel, predominantly of siliceous particles in a sandy, ferruginous matrix. Sandy and coarse conglomeratic facies were noted at the head of Nuevo Canyon.

Only a small fraction of the upland was examined for gravels, and it is probable that later detailed studies will find residuals to be widespread over much of the range.

The regional relations of the conglomerate and gravels to the quartzose conglomerate in the Pecos lowland (Meinzer *et al.*, 1927, pp. 9–10; Fiedler and Nye, 1932, pp. 35–38) and to Ogallala gravels of the High Plains indicate that a unit deposit filled an ancestral Pecos lowland and spread out over adjoining uplands as an extensive Tertiary cover over most of the Pecos section (Bretz and Horberg, 1949).

In the Carlsbad Caverns region this conclusion is supported by the occurrence of siliceous gravel residuals of similar lithology at all levels between exposures of quartzose conglomerate in the lowland and the summit of the range (fig. 3). Many occurrences doubtless represent re-worked Ogallala materials, but those at high elevations on the Guadalupe Range and the flanks of the Sacramento Range to the north approximate or lie above the projected High Plains surface; those at lower elevations occur on erosion surfaces, which indicate older gravels in the ranges as sources.

[4] C. C. Branson, personal communication, 1947.

[5] B. T. Gale, personal communication, 1949.

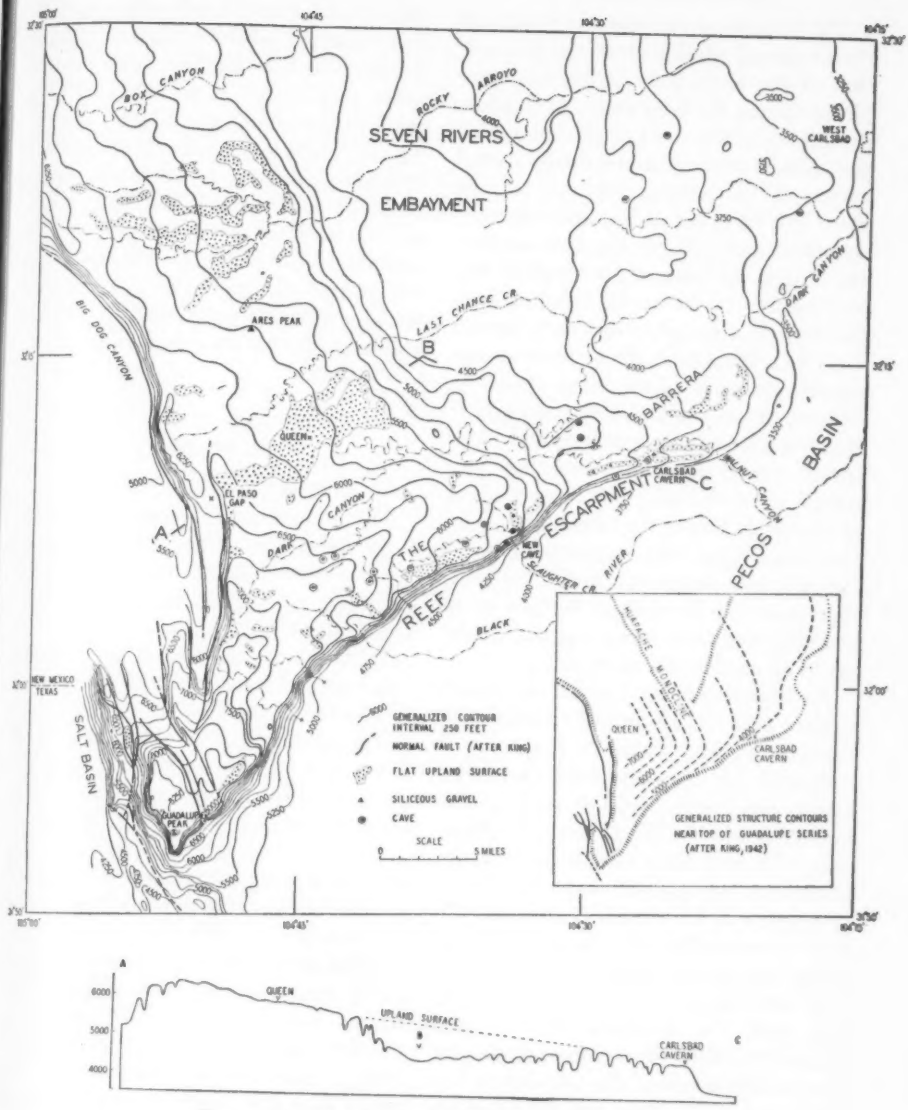


FIG. 2.—Generalized contour map of the Guadalupe Range

AGE AND CORRELATION

The gravels of the summit plain and their regional relations indicate that erosion of the surface probably was completed during the later stages of Ogallala deposition as the sheet of alluvium filled the lowland to the east and finally spread across the Guadalupe upland. If the plain had been cut earlier and dissected by streams on the pre-Ogallala surface, the critical evidence of pre-Ogallala valleys preserving valley fill has not been discovered. If the plain had been formed in post-Ogallala time, the transverse consequent drainage of the range would be difficult to explain, and also it is unlikely that the filled solution cavities and widespread gravel residuals would be preserved so extensively. The occurrence of remnants of Lower Cretaceous strata in the area suggest that important truncation of strata occurred in pre-Cretaceous time and that the present surface could have resulted from refaceting and lowering of an earlier extensive plain.

A correlation of the Guadalupe upland surface with the Sacramento plain in the Sacramento Mountains to the north is suggested by its comparable elevations above the Pecos lowland and similar gravel residuals (Bretz and Horberg, 1949). Uncertainties arise because of the absence of topographic maps for the region north of the Carlsbad area and the lack of knowledge of the tectonic history of the Sacramento Range.

A correlation of the Guadalupe surface with the Diamond A–Mescalero plain of the Roswell area is suggested by comparable levels of the Guadalupe upland north of Carlsbad and the Mescalero plain, 10 miles to the northeast (Oil City quadrangle). The projected levels lie about 175 feet above Pecos River. This approximates the 150-foot terrace in the area just to the north (Meinzer *et al.*, 1927, p. 6) which has been correlated with the Diamond A–Mescalero surface. It is believed, however, that the upland surface near Carlsbad has been reduced below original levels, as indicated by a break in slope north of Carlsbad Caverns (fig. 2). These lower uplands are not sufficiently uniform to warrant correlation with the Diamond A–Mescalero plain, and their accordance with that surface probably is coincidental. Correlation of the unreduced Guadalupe surface with the Mescalero plain would imply that the Mescalero is also an exhumed pre-Ogallala surface.

VALLEY FILL IN THE PECOS LOWLAND

QUARTZOSE CONGLOMERATE

The quartzose conglomerate of the Pecos depression is well known from exposures in the Roswell Basin (Meinzer *et al.*, 1927, pp. 35–38; Fiedler and Nye, 1932, pp. 35–38; Morgan, 1938, pp. 14–15), and the same deposit with similar lithology and structural relations is widely exposed in the Caverns area. Numerous exposures occur along the Pecos River, and more or less continuous ledges are present along the lower Black River for a distance of almost 30 miles (fig. 3).

The deposit is a firmly cemented conglomerate, composed largely of limestone pebbles but containing abundant foreign siliceous pebbles. The siliceous pebbles, in order of abundance, consist of quartz, chert, and quartzite. Granite, rhyolite, schist, basic igneous, and sandstone pebbles are minor constituents. Interbedded siltstone and sandstone were noted at a few localities. The exposures along Black River show increasing percentages of limestone and coarse material westward toward the mountain front. One of the best-exposed sections of the conglomerate in the area at Telltale

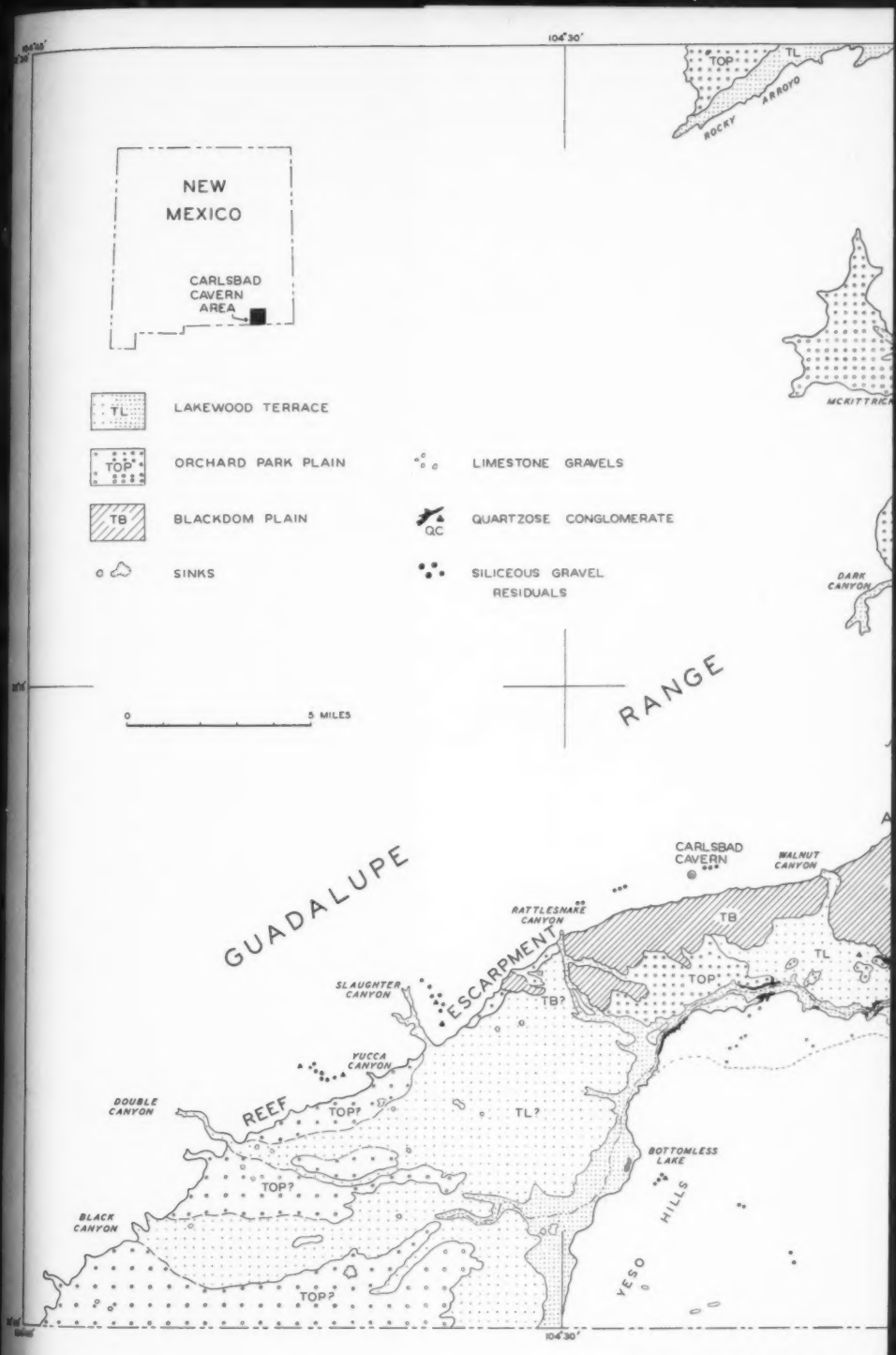
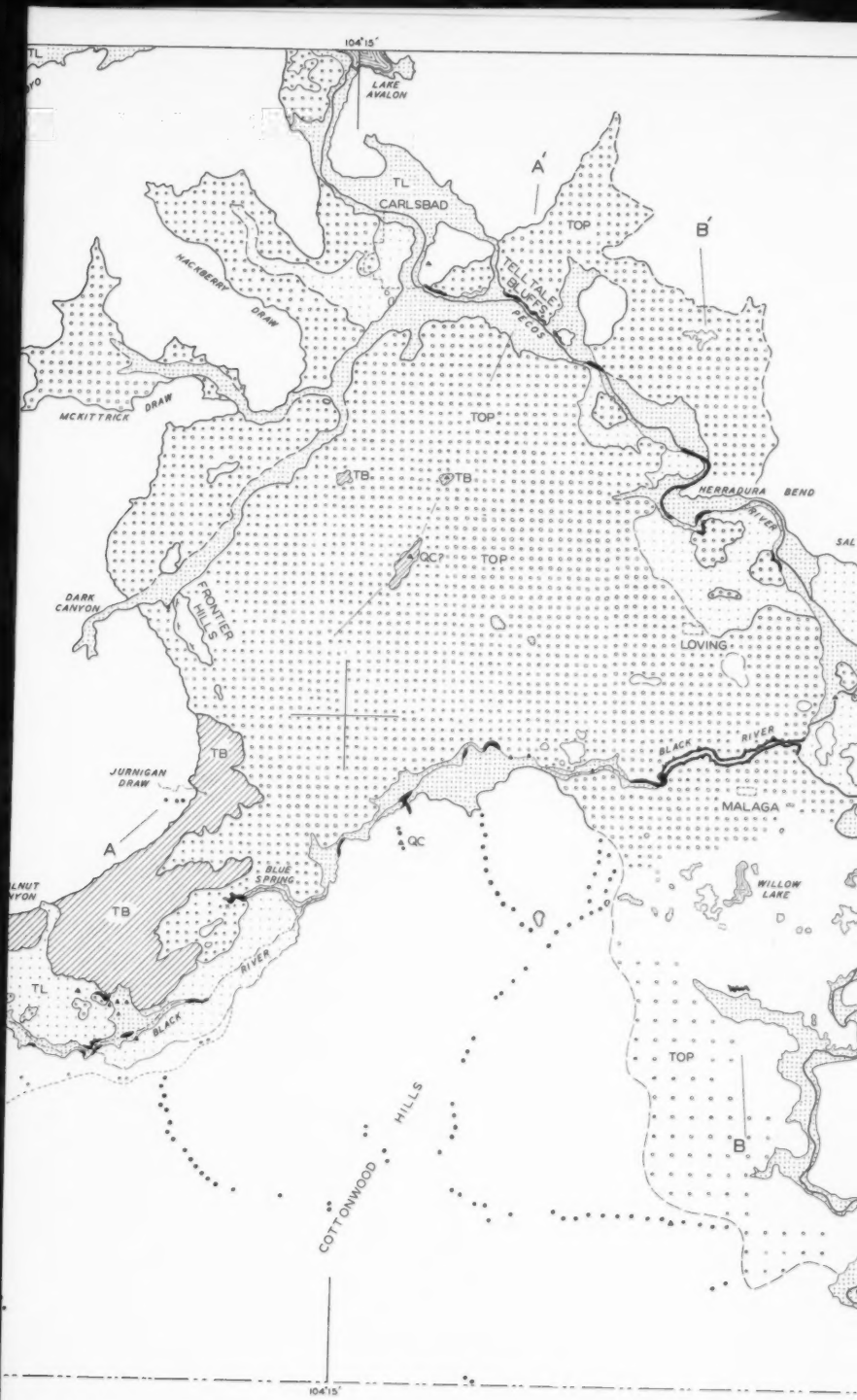
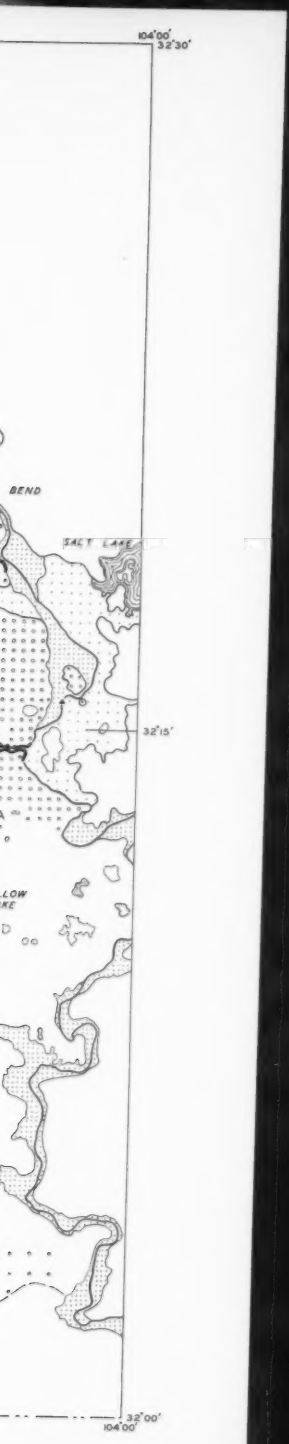


FIG. 3.—Erosion surfaces in the C



ces in the Carlsbad Caverns area


104°00'
32°30'
BEND
SALT LAKE
32°15'
32°00'
104°00'

Bluff along Pecos River, 3 miles southeast of Carlsbad (fig. 3), is described in table 1.

Wherever the conglomerate is well exposed it shows evidence of disordered tilting, faulting, or downwarping with The lack of structural continuity, the existence of recent sinks, and the presence of underlying evaporites point to solution-collapse as the cause of deformation.

Drillers' records of about fifty irrigation wells[6] in the area between Carlsbad

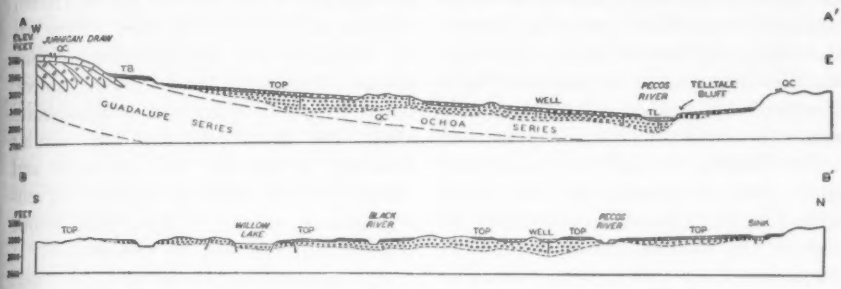


FIG. 4.—*A*, cross section along *AA'*, fig. 3; *B*, cross section along *BB'*, fig. 3

TABLE 1

QUARTZOSE CONGLOMERATE AT TELLTALE BLUFF ALONG PECOS RIVER
S.W. COR., SEC. 11, T. 22 S., R. 27 E.

DESCRIPTION OF ROCK	THICKNESS (FEET)	
	Unit	Cumulative
1. Caliche caprock, light-gray, dense, irregular layers, brecciated, concretionary; isolated siliceous pebbles and traces of limestone pebbles	3½	3½
2. Limestone-pebble conglomerate with chalky caliche cement and coatings; white; average diameter about 2½ inches; siliceous pebbles	8	11½
3. Limestone-pebble conglomerate, gray, dense, breaks across pebbles, irregularly bedded in channels and in low foresets; abundant siliceous pebbles; locally channeled into underlying silt	14	25½
4. Silt, red to brown, horizontally stratified; sandy, gravelly; pebble bands; abundant siliceous grains and pebbles; evidences tilting and minor faulting; rests with angular unconformity on underlying Permian limestone	26	51½
5. Limestone bedrock (Permian), dips steeply to southeast	.....	.....

dips up to vertical (pl. 1, *B*). At two localities along Black River (N.E. ¼, S.W. ¼, sec. 12, T. 25 S., R. 25 E.; S.E. ¼, N.E. ¼, sec. 8, T. 24 S., R. 28 E.) local collapse by subsidence is indicated by centripetal dips. The Permian bedrock appears to be even more deformed, and this deformation in most places is disconformable rather than conformable with that of the overlying conglomerate.

and Malaga show that the conglomerate has a maximum thickness of over 200 feet. The materials penetrated include important thicknesses of sand, gravel, and conglomerate but reveal a higher proportion of silt than is indicated by surface exposures. The deepest part of the fill is continuous just to the west of

[6] Kindly provided by H. P. Burleigh, U.S. Soil Conservation Service, Carlsbad, N.M.

the present river, and there also appears to be an extension of deep fill westward along the present course of Cass Draw. The fill terminates south of Malaga, where bedrock is continuous across the floor of the present valley, and it is also separated by a bedrock barrier north of Carlsbad from a fill of somewhat greater thickness in the Roswell Basin. These relations indicate, as in the Roswell Basin (Morgan, 1938, pp. 11–12), that the depression in which the fill is now preserved is due largely to solution-subsidence rather than to erosion by the Pecos River. The subsurface data show that the base of the conglomerate was downdropped over 100 feet by subsidence. The continuity of the fill, however, suggests that most active solution may have occurred along the axis of former surface valleys.

There is no definitive evidence of the age of the quartzose conglomerate, as no fossils have been found. Previous writers (Meinzer *et al.*, 1927, p. 7; Fiedler and Nye, 1932, pp. 109–113; Morgan, 1938, pp. 14–15) tentatively considered it early Pleistocene. Its relations to high-level gravels in the area and along the Pecos lowland, north as far as Santa Rosa, however, indicate that it may represent a basal facies of the Pliocene Ogallala formation (Bretz and Horberg, 1949).

GRAVEL RESIDUALS IN THE PECOS LOWLAND

Siliceous gravel residuals above the level of exposures of quartzose conglomerate are widespread throughout the Pecos lowland (Bretz and Horberg, 1949). Within the area they occur in the mature uplands south of Black River at elevations ranging up to 4,700 feet (aneroid). The siliceous pebbles are similar in lithology to those in the quartzose conglomerate and the residuals in the Guadalupe Range. Limestone-pebble conglomerate with siliceous pebbles, found *in situ* at the northern end of the Yeso Hills (cen. sec. 12, T. 26 S., R. 24 E.) and at the north edge of upland (S.E. ¼, N.E. ¼, sec. 19, T. 24 S., R. 27 E.) (fig. 3) doubtless represents the parent-deposit from which the scattered siliceous pebbles were derived. At the latter locality the conglomerate occurs about 1 mile from, and 150 feet above, tilted ledges of quartzose conglomerate along the Black River. The similar lithology of the two conglomerates and the presence of residuals in the intervening area are strong evidence that a unit deposit once covered the entire area.

An isolated occurrence of debris composed of Washita (Lower Cretaceous) sandstone and fossiliferous limestone at the north end of the Yeso Hills (cen. N. ½, sec. 31, T. 25 S., R. 25 E.) is reported by Lang (1947, pp. 1472–1478). This material differs from the conglomerate, and associated siliceous pebbles are clearly differentiated from it. The material is believed to have been let down in a solution channel in the Permian fore-reef evaporites from once overlying basal Cretaceous beds. Cretaceous fossils in float in the Guadalupe Range and patches of sandstone near Jurnigan Draw also are reported by King (1942, p. 640).

PIEDMONT PLAINS AND TERRACES

BLACKDOM PLAIN

Remnants of the Blackdom plain occur as a frayed upland along the mountain front between Dark Canyon and Slaughter Canyon (fig. 3). The surface where it is best preserved slopes eastward at a gradient of about 50 feet per mile and is about 75 feet above Black River drainage. Northeast of Walnut Canyon the surface is bordered on the east by the Orchard Park plain and at many places

is separated from it by a scarp 25–40 feet high. Southwest of Walnut Canyon the surface is extensively eroded, and its outer boundary is not so clearly defined.

The surface is underlain by limestone gravels which have a well-developed caliche caprock. Along the mountain front near Jurnigan Draw the gravels rest on a beveled bedrock surface. At the outer margin of the surface near the mouth of Walnut Canyon and Blue Spring, however, the areal relations indicate that the limestone gravels rest on a surface which truncates tilted quartzose conglomerate (fig. 3).

Scattered sinkholes and a fault in the limestone gravels near the mouth of Jurnigan Draw are evidence that some solution-subsidence followed formation of the plain.

ORCHARD PARK PLAIN

The Orchard Park plain is represented by a great, undissected, fan-shaped surface which has its apex in a re-entrant of the mountain front near the mouth of Dark Canyon, and by smaller terrace remnants along Pecos River, Black River, and Rocky Arroyo (fig. 3). The extensive surface heading in the Dark Canyon re-entrant has an eastward slope of about 45 feet per mile and near the city of Carlsbad is 30–40 feet above the Pecos River. Most of the irrigated land in the Carlsbad Basin is on this surface. The related terraces east of the Pecos are 30–50 feet above drainage, and those along Black River are 25–75 feet.

The surface of the plain is covered by brownish soil and alluvium, which in most places overlie calichified limestone gravel. The caliche zone does not appear to be so strongly developed as on the Blackdom gravels. Sandy and silty beds interbedded with the gravel were noted at a few localities. An exposure of the gravel along Pecos River at the east end of Wildcat Bluff (Carlsbad quadrangle) shows northeast-dipping foreset gravels, channel gravels, sand lenses, and interbedded brown silt and sand. Here and at several other localities south along the Pecos and along the Black River, the gravels overlie deformed ledges of quartzose conglomerate (pl. 1, *B*).

The thickness of the limestone gravel, as far as can be determined from exposures and well records, is not more than 50 feet and probably considerably less. This is also suggested by several islands of quartzose conglomerate and bedrock which rise above the level of the plain.

The uniform surface of the main plain is modified by shallow draws leading from canyons in the mountains; by Cass Draw, a broad depression on the plain; and by scattered shallow sinks. South of Black River the southward extension of the surface is interrupted almost completely by an area of recent solution-subsidence centering around Willow Lake (Malaga quadrangle). Beyond this area the surface continues south as a less uniform gravel-covered plain surrounding numerous residuals of older topography. To the west it merges with broad gradual slopes on bedrock in the adjoining uplands. Along the north flank of these uplands remnants of limestone gravels, derived from the Guadalupe Range to the west, were noted up to elevations of 100 feet above Black River (fig. 3).

GRADED PLAINS SOUTH OF BLACK RIVER

The graded plains in the mature uplands south of Black River merge with the Orchard Park plain on the north and east (fig. 3) and probably belong to the same cycle of erosion. The plains conform to present drainage lines and have concave profiles which break rather abruptly with clusters of residual hills, i.e.,

Cottonwood Hills and Yeso Hills (pl. 1, *C*). The slopes, in general, range from 75 to 100 feet per mile. In many places the surface clearly truncates bedrock structure, and it is probable also that locally the surface extends across fills in sinks and possibly across outliers of quartzose conglomerate. Youthful dissection is shown by the larger valleys and numerous arroyos slightly entrenched below the level of the plains. Recent sinks are not so conspicuous as they are in adjoining areas.

ORIGIN OF PIEDMONT PLAINS

The erosional, rather than constructional, origin of the Orchard Park plain is indicated by (1) the probable thinness of the gravel cover; (2) the beveled surface on deformed underlying bedrock and quartzose conglomerate; (3) the islands of quartzose conglomerate and bedrock surrounded by limestone gravels; and (4) the gradation of gravel-covered surfaces with gently sloping rock plains in the upland south of Black River. A similar origin for the Blackdom plain is suggested by characteristics 1 and 2. In the Roswell Basin the correlative surfaces were considered by Fiedler and Nye (1932, pp. 106–109) to be largely constructional features; but later Morgan (1938, p. 14), because of the thinness of the gravel cover, concluded that they were cut surfaces on older deposits.

The plains were graded to successively lowered base levels of the Pecos River and were formed on the weak Permian rocks and older valley fill of the lowland by streams from the mountains to the west. There was no retreat of the resistant Reef escarpment forming the mountain front; but, by the coalescence of cut plains and rock fans, the weaker sediments were effectively removed from the escarpment. The facts (1) that most extensive surfaces are related to the largest drainage lines in the mountains, (2) that the surfaces are restricted to soft rocks, and (3) that there has been no back-wasting of the mountain front indicates that lateral planation by streams was the dominant process.

The term "pediment," as now used (Bryon and McCann, 1936, pp. 148–152; Cotton, 1942, pp. 29–35), includes surfaces of this type, even though many "type" features assumed in some discussions are absent. The graded plains in the uplands south of Black River are restricted to drainage lines and might be termed "partial pediments." It is recognized that no clear distinctions can be drawn between plains of lateral planation, local peneplains on soft rocks, and the pediments as here described, so that a full discussion of the problem would be unwarranted in the present paper.

LAKEWOOD TERRACE

The Lakewood terrace is 15–30 feet above present drainage lines and is essentially continuous along the Pecos Valley (fig. 3). It also is recognized along Rocky Arroyo and with less certainty along upper Black River. Along smaller

PLATE 1

A, Truncation of Permian limestones by the Guadalupe upland surface on south side of upper Black River Canyon. View south from Dark Lookout, Carlsbad Caverns West quadrangle.

B, Deformed quartzose conglomerate underlying undeformed limestone gravels along Black River, 3¼ miles southeast of Carlsbad Caverns. Cut along U.S. Highway 62, Carlsbad Caverns East quadrangle.

C, Graded slopes and residual hills south of Black River, 8 miles west of Malaga (Malaga quadrangle). View south from Black River Valley.

A

B

C

Guadalupe upland surface, graded plains south of Black River, and deformed quartzose conglomerate.

tributaries it merges with recent alluvium. Slightly higher levels, up to 40 feet above drainage and 10–20 feet above the normal Lakewood, are represented by abandoned Pecos channels surrounding outliers of the Orchard Park plain.

The deposits underlying the terrace were noted at several localities along the Pecos and are composed almost exclusively of red-brown silt and silty sand.

PIEDMONT PLAINS SOUTH OF RATTLESNAKE CANYON

The piedmont plains fronting the mountains southwest of Rattlesnake Canyon (fig. 3) are more complex than those previously described, and their genesis and correlation are less certain. Superficially they appear to represent a series of piedmont alluvial fans in various stages of dissection. The underlying limestone gravels appear to be thick, and bedrock exposures of the fore-reef facies are limited to a few areas just in front of the Reef escarpment.

The plains, however, are not typical bajadas, in that the higher fan-shaped accumulations are in the interstream areas and are separated by youthful graded plains and valley strips which head at the mouths of major canyons. Two types of topography thus are present: the youthful plains along larger streams and the more dissected interstream areas. In places they are separated by definite scarps, and opposite Double Canyon an island remnant of the higher fan surface with a west-facing scarp is surrounded by lower valley strips. The lower surface is most extensive opposite Slaughter Canyon, where a broad sloping plain covers an area of several square miles. The average gradient of the lower surface is about 100 feet per mile and that of the higher, which is slightly steeper, about 110 feet per mile.

The lower surface merges with the present floodplain of Black River or is separated from it by a low scarp. This, together with the fact that it is slightly entrenched by present draws, suggests a correlation with the Lakewood terrace. The higher dissected plain, which is intermediate between the lower plain and remnants of the Blackdom surface to the north, could be considered equivalent to the Orchard Park plain.

The restriction of the lower plain to present major stream courses with the development of valley strips indicates origin by lateral stream planation, and the surface could be considered a partial pediment. The origin of the higher plain is less certain, as no evidence of beveling of older fill was noted. This evidence, however, could have been missed in the reconnaissance traverses made across the area and may be revealed by more detailed studies.

Numerous sinkholes, many with recent-appearing rims, are present on both surfaces.

CORRELATION AND AGE

The recognition of Blackdom, Orchard Park, and Lakewood surfaces in the area is based on relative elevations and their essential continuity along the Pecos and is believed to be strongly supported. Remnants of the higher Diamond A–Mescalero plain on the 150-foot terrace along the Pecos near the mouth of Rocky Arroyo (Meinzer *et al.*, 1927, p. 6) were not recognized in the area. The Mescalero plain, however, is extensive in the adjoining region east of the Pecos.

Tentative age assignments of surfaces in the Roswell area were made by Nye (Fiedler and Nye, 1932, p. 112) as follows: the Blackdom terrace to the Sangamon interglacial stage; the Orchard Park to the Peorian interglacial substage; and

the Lakewood to a postglacial arid substage. Although the over-all Pleistocene age of the surfaces is evidenced by their regional relations to the Pliocene Ogallala formation, further correlations appear unwarranted. It is uncertain whether the surfaces were determined by diastrophic movements or by Pleistocene climatic changes; if they were climatically controlled, it is also uncertain whether erosion or aggradation occurred during the humid pluvials. Nye's concept of alternation of erosion and aggradation is based on the interpretation of the piedmont plains as constructional features. If, instead, these features are erosional, as proposed by Morgan (1938, p. 14) and in the present study, successively lowered, rather than fluctuating, base levels are indicated.

DRAINAGE EVOLUTION

GUADALUPE RANGE

The major northeast-flowing streams are consequent on the tilted surface of the fault block and in their lower courses are transverse across the Reef escarpment (Lang, 1937, pp. 896–898) (fig. 2).

Transverse drainage is especially notable in the cases of Rocky Arroyo and Last Chance Creek, which flow down the slope of the northwest prong of the limestone upland, cross the weak beds in the Seven Rivers lowland, and, instead of continuing north on the weak beds, cut through the east prong of the limestone upland to enter the Pecos.

Southwest of Slaughter Canyon the northeast consequent pattern gives way to a series of parallel short canyons, which drain southeastward normal to the Reef escarpment. Even in these canyons, however, the northeast trend is shown by tributary canyons, which almost exclusively drain northeast. Many of the canyons (i.e., Last Chance, North and South McKittrick, and Pine Spring) are beheaded by faults at the western scarp of the range. Dog Canyon drainage, at the base of the western scarp, follows a series of three tectonic depressions.

All the longer, northeast-trending canyons are characterized by incised meanders, largely of the ingrown type. Most striking examples are the Serpentine Bends of Dark Canyon (Carlsbad Caverns West quadrangle). The shorter, southeast-trending canyons in a few places have meander patterns of much smaller scale.

The accordance of major streams with fault-block structure and the tilted upland surface indicates that initial drainage formed during an early stage of block-faulting, or possibly along the axis of a monoclinal fold close to the present fault scarp. The transverse drainage is independent of secondary structures within the range and cannot be explained by headward erosion of subsequent streams or by antecedency. It is most logically explained by superposition, and the gravel residuals evidence an unconsolidated cover suitable for this process. The southeast drainage in the southern part of the range resulted largely from removal of weak beds fronting the Reef escarpment and in part from uplift along the Reef escarpment. The uplift is shown by abnormal dips along the escarpment (Lang, 1937, pp. 892–895; King, 1942, p. 587) and by southeast drainage trends in the Pecos lowland in the southern part of the area. Drainage of the southern tip of the range is directly southeast by way of Delaware River; farther north, southeast drainage appears to have been captured by headward erosion of Black River.

As the result of later block-faulting the initial consequent streams became entrenched and superimposed, incised me-

anders were formed, and Tertiary cover was stripped away except for scattered residuals.

PECOS LOWLAND

The Pecos depression is believed to have been produced by uplift of the ranges to the west, by solution-subsidence along a series of troughs, and to a minor degree by headward erosion (Lee, 1925; Lang, 1937, pp. 896–898; Morgan, 1942, pp. 27–35). Two stages, the present and a prequartzose conglomerate (Ogallala) stage, are indicated, and it is probable that the same factors apply to both. The major episodes of solution-subsidence shown by deformation of the bedrock formations and quartzose conglomerate occurred before and after deposition of the conglomerate. As a result of this solution and collapse, much of the soluble material underlying the lowland must have been removed because the overlying limestone gravels of the piedmont plains are undeformed except for minor recent sinks.

The present position of the Pecos within the area appears to be determined largely by later subsidence along the trend of the deepest fill of quartzose conglomerate. It may have been shifted slightly to the east of this fill by detritus which was shed from the mountains during erosion of the Orchard Park plain. As previously noted, upper Black River drainage probably is due to piracy of southeast-flowing consequents. The abundance of sinks in this area suggests that solution-subsidence was an important factor here also.

TIME OF CAVERN DEVELOPMENT

A study of seven caves in the Guadalupe Range clearly shows that they are older than the present topography, including both the present canyons and the much older upland surface (Bretz, 1949). This conclusion is based in large part on the following lines of evidence: (1) cavern passages transected by present canyon walls and upland surfaces, as revealed by present openings to the surface and more often by passages filled and choked off by debris; (2) caverns incommensurate in size with present drainage basins; (3) dripstone and flowstone deposits that are too large to be explained by the present thickness of overlying rock and drainage area; (4) dripstone and flowstone in surface rubble; and (5) features of the caverns indicating an early phreatic and later vadose stages in their history (Bretz, 1949).

The geomorphic relations thus indicate that the caves are among the oldest features in the area. Their intersection by the upland surface and the presence of gravel-filled solution cavities on summit areas indicate that they were formed either before or during an early stage of the Ogallala cycle. Their vertical range implies considerable relief in an earlier cycle, and the integration of subsurface drainage into the enormous passageways of Carlsbad Caverns indicates that the cycle reached a mature stage. These conditions appear to be fulfilled in large part by the Ogallala cycle of aggradation and an earlier cycle of erosion: the caves were initiated by phreatic circulation under a pre-Ogallala surface of important relief and became integrated into large passageways below the Guadalupe upland at a mature stage in the cycle; their upper galleries were transected as the upland surface was cut to lower levels toward the close of the cycle, and openings to the surface were filled with gravel as the rising Ogallala deposits covered the upland; the complex vadose cavern history of dripstone and flowstone deposits, roof collapse, and stream activity transpired as the Ogallala fill was re-

moved from the lowland under the control of progressively lowered base levels of Pecos River.

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THE OGALLALA FORMATION WEST OF THE LLANO ESTACADO[1]

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ABSTRACT

Gravel remnants at various elevations over a wide area in southeastern New Mexico are related to a once extensive cover of High Plains Ogallala deposits. A correlation of the "quartzose conglomerate" fill along the Pecos depression with basal Ogallala is suggested.

INTRODUCTION

The Llano Estacado or Staked Plains of southeastern New Mexico and northwestern Texas constitute a clearly defined physiographic unit, rising above surrounding country by a marked scarp for almost its entire margin except the southern. This high, floorlike plain of 20,000 square miles is the but slightly modified surface of the Ogallala formation (Darton, 1898, pp. 732–742), generally regarded as largely of Pliocene age. Except for broad, shallow sinks, slightly entrenched stream courses, and some dune tracts, it is as featureless as when it was made.

The Ogallala formation of the Llano is not, however, of uniform thickness. A buried topography, chiefly in Triassic rocks, is expressed in thicknesses which range from a few tens of feet over pre-Ogallala hills and ridges to more than 400 feet in New Mexico and 550 feet in Texas over buried valleys.

Identified from Nebraska to Texas, the Ogallala formation, or group of formations, has been universally interpreted as a fluviatile apron deposited east of the Rocky Mountain front, the stream-transported waste containing minor members of eolian and lacustrine origin. The Llano Estacado portion, however, lies well to the southeast of the nearest southern Rocky Mountain range, the crystalline-cored Sangre de Cristos of Colorado and northern New Mexico. The mountain units of the Basin and Range Province, lying directly west of the Llano, are the Sierra Blanca, Jicarillos, and Capitan mountains of porphyritic lavas and the Sacramento and Guadalupe mountains of limestone. Most of the abundant quartzite, jasper, and vein quartz pebbles in the Ogallala of the Llano must have traveled southeasterly to reach their resting place. The general southeasterly slope of the Llano, averaging 10–15 feet to the mile, therefore appears to be the original depositional slope.

The western margin of the plateau-like plain is a scarp ranging up to 200 feet in height, slightly nicked in places by short westward-draining ravines but with its summit generally constituting a divide between the south-flowing Pecos on the west and the slightly entrenched easterly drainage of the plain's surface. In effect, this western margin is a low cuesta. Locally, buried hills of Triassic rocks appear in the retreating scarp, but for most of its length the Ogallala formation extends to the base.

The Pecos River, heading in the Rincon and Truchas ranges at the south end of the Sangre de Cristos, lies 12–40 miles west of the scarp and 300–1,000 feet lower. Several isolated areas of Ogallala,

[1] Manuscript received April 27, 1949.

shown on the geologic map of New Mexico (Darton, 1928), lie west of the Pecos in the northern latitudes of the Llano (fig. 1). The largest one covers approximately ten townships. So far as the authors have seen, there are no scarped boundaries to these areas. South of these tracts, no Ogallala is mapped west of the Pecos for the 150 miles to New Mexico's southern boundary. It is generally believed, however, that the formation, before Pecos River erosion, extended west to these southern New Mexican ranges (Sellards *et al.*, 1943, p. 770).

This paper presents field evidence that the Ogallala formation once extended southward on the west side of the river at least to the Texas line, that Pecos drainage has removed it, save for a few small patches and widely distributed residual quartzose pebbles, and that the "quartzose conglomerate" in the bottom of the Pecos Valley is probably basal Ogallala instead of an early Pleistocene valley deposit.

The lithology of the Ogallala formation underlying the Llano plain has been described repeatedly as a complex series of gravels, sands, silts, and clays; the number of beds, the thicknesses, the sequences, and other characters varying so much from place to place that, in the lack of fossils contemporaneous with the deposition, even a generalized stratigraphic column has rarely been attempted.[2] The deposit is believed to have originated as a great alluvial plain or bajada on which various mountain-born streams debouched, deposited, wandered, divided into shifting distributaries, probably had temporary floodplain lakes, and probably provided the fines for associated wind transportation and deposition in the changing interstream areas. Some authors describe the basal portion as containing considerably more and coarser gravel than the remainder of the section; all recognize that a country of hills and valleys was invaded and eventually buried. Several recognize that the siliceous pebbles must have been contributed from mountains to the northwest and that the limestone pebbles came more largely from the west. Varying proportions of siliceous and calcareous constituents indicate shifting alternations of stream channels from the two contrasted source areas.

Induration of the Llano Ogallala is only partial. Calcite-cemented members are, by some, termed "caliche." That term, however, should be reserved for the most completely altered portion, the "caprock," which is interpreted by some as the uppermost sedimentary member of the formation, by others (including the authors) as an alteration product made in post-Ogallala time.

The surface of the Llano Estacado, the slopes of its bounding scarps, the deposits at scarp bases, and the exhumed lower country in front of them carry siliceous pebbles in places. A clear inference is that these pebbles are residuals and re-worked deposits from reduction of the Llano, surviving after disappearance of the matrix and associated calcareous pebbles of gravelly members, as the surface has been lowered by weathering and the scarps have been erosionally driven back from adjacent lowlands. In many places the siliceous pebbles are being released, by weathering, from the caliche caprock.

During nearly 2,000 miles of traverses on the Pecos lowland and Llano upland, ten crossings of the marginal scarps were made, seven of the western scarp, two of the eastern, and one of the northern. In all these crossings, gravel members or

[2] See Sellards *et al.*, 1933, pp. 767–771, for summary.

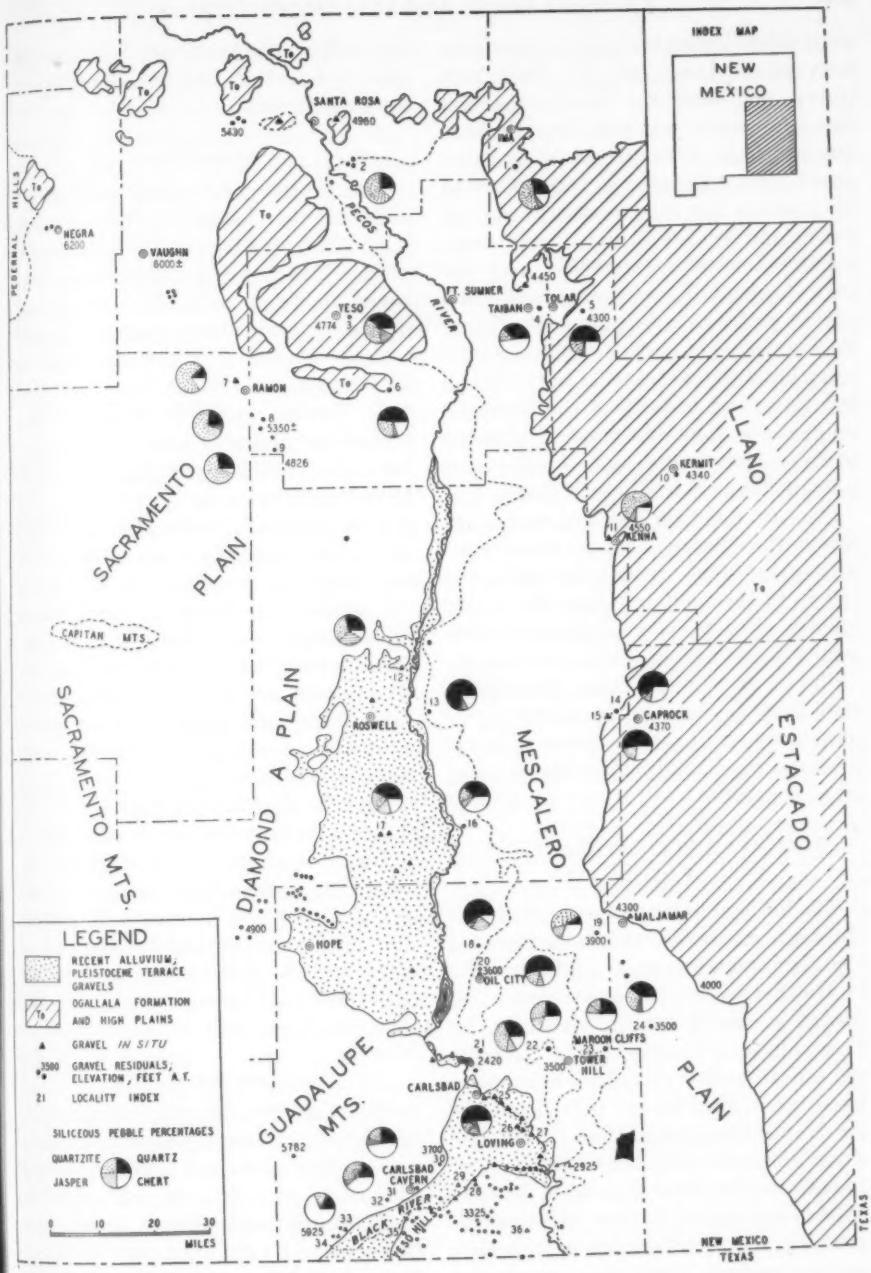


FIG. 1.—Ogallala formation and siliceous gravel residuals in southeastern New Mexico

slope debris showed pebbles of quartzite, vein quartz, jasper, granite, chert, porphyry, and lava, the siliceous pebbles being far more abundant than those of igneous rock, some strata being composed almost entirely of them. Carried by drainage from the western scarp and left behind by cliff retreat, these foreign pebbles are widely scattered over the Pecos lowland. The authors found 38 localities where they lie above all existing Pecos terraces but below and beyond the scarp bases (fig. 1). Most localities are on hill slopes and summits of the lowland's rough topography, and none was counted where modern drainage could have brought the pebbles from the scarp.

Because the regional slope, southward along the Pecos and southeastward across the Llano, ranges through 1,650 feet in the lowland and 2,000 feet in the upland, altitude figures for these pebble localities are meaningless unless map coordinates accompany them. The significant item is the relative altitude of a locality in the lowland above adjacent drainage ways and below the near-by scarp summit.

OGALLALA AND RELATED GRAVELS EAST OF PECOS RIVER

The lowland between Pecos River and the scarp, exposed by eastward retreat of the Llano margin, ranges up to 40 miles in width and for the most part is included in the Mescalero plain (fig. 1). Low cliffs and cuestas of tilted Triassic red sandstone in its relief are believed to have been inherited, in part, from the pre-Llano topography. More striking are sinks and saline lagunas formed since the exhumation. Red dune-sand deposits (Mescalero sands, Darton and Reeside, 1926, fig. 1, p. 413) also are of postexhumation origin. The linear draws and basins of this Triassic lowland parallel the strike and genetically are rows of sinks rather than stream-made valleys of the present cycle.

TOWER HILL

One of the most pronounced strike cliffs of the lowland is the Livingston "Ridge"–Maroon Cliffs–Nimenim "Ridge" scarp, lying about midway between the river and the Llano scarp and possessing more than 200 feet of relief between its summit and the sinks in Clayton Basin and Nash Draw, just west of it. During retreat of Maroon Cliffs, several isolated hills have been left behind, Tower Hill (Clayton Basin and Nash Draw quadrangles; fig. 1), 20 miles northeast of Carlsbad, being one. This hill's summit is 2 miles from the cliffs and 50 feet lower, but more than 100 feet above the intervening country. Thick, dense caliche caps the hill and covers at least the southern slope. Scattered through this caliche are good-sized pebbles of chert, jasper, and quartzite. Twenty-five miles to the northeast is the Llano scarp, its base less than 300 feet higher. Cuts along U.S. Highway 62, between Tower Hill and the Llano, show similar pebbles at intervals as far east as Laguna Gatuna. The easternmost exposure (locality 24, fig. 1) is of a gravel deposit *in situ*, most of its pebbles composed of limestone. The altitude here is no higher than the top of Maroon Cliffs, 500 feet below the Llano plain, 10 miles distant.

FADEAWAY RIDGE

This "ridge" (Oil City quadrangle; fig. 1) is an east-facing slope descending 200–250 feet to Burton Flat and having Clayton Basin still farther east, with its sink bottoms another hundred feet lower between it and the Nimenim "Ridge." Most of the Nimenim cliff brink is lower than the top of the Fadeaway slope. The

Llano scarp base, 30 miles to the east, is about 400 feet higher. The upland above and west of the Fadeaway slope is a little plateau 4–5 miles wide, the surface dropping off over Chalk Bluffs and McMillan Escarpment to the Pecos River, about 4 miles distant and 300–350 feet lower.

The surface of this plateau is sprinkled in places with siliceous pebbles, the altitudes ranging between 300 and 400 feet above the Pecos and the same distance below the scarp base, 25 miles to the east.

CAPROCK

The Mescalero plain east of Roswell (fig. 1), lying between the river and the Llano scarp, carries much eolian sand, and only one locality of siliceous pebbles was found, about 12 miles east of the river. The pebbles lie scattered on the surface and embedded in a caliche deposit about 375 feet above the Pecos and nearly 500 feet below the scarp base, 25 miles distant.

This lowland should have an abundance of such pebbles, for the cliff near the top of the scarp has the largest outcropping of siliceous pebbles that the authors saw in the western Llano scarp (locality 15, fig. 1). Gravel layers up to a foot thick in a brown silt are composed almost wholly of quartzose pebbles. An associated, firm, dense limestone layer also carries scattered siliceous pebbles, though no grouping into seams was found. This limestone has a curious nodular texture, the nodules tending to be of uniform sizes along any given stratum plane. They are thought to be traces of limestone pebbles, the original gravel at this level having had only a small percentage of foreign material.

Scattered, broken siliceous pebbles lie in the soil on the top of the scarp, released during disintegration of the caprock caliche. The authors hope to show, in another paper, that the caliche itself is a weathering product of earlier and different climatic conditions. If so, the scattered pebbles, before incorporation into caliche, came from vanished gravelly members lying somewhat higher than the present Llano surface.

KENNA AND KERMIT

One of the larger breakdowns of the Llano's western scarp is utilized by the Santa Fe Railroad and U.S. Highway 70 to cross the declivity between Kenna and Kenna Gap. It is wide and smoothly floored but has a very limited contributing drainage area. Sinks on top near the gap suggest that the breakdown may be largely of sink origin.

Members of the Ogallala formation are exposed in a highway cut near the bottom of the grade (locality 11, fig. 1), and a surficial caliche deposit is opened in a subsummit pit in the slopes of Kenna Mesa to the north.

Quartzose pebbles dominate over limestone in the gravel of the highway cut and are rare in the caliche exposed in the hillside pit. But, at Kermit station on the top of the Llano, 15 miles northeast of the Gap and 300 feet lower (down the dip slope), fairly large siliceous pebbles are embedded in the caliche of the plain's surface (locality 10, fig. 1). Like those at Caprock, they are taken to record the weathering-away of a dominantly limestone gravel whose calcareous content has made the caliche.

TOLAR

Tolar lies in the largest erosional interruption of the Llano's western scarp (fig. 1). More than 150 square miles of the summit plain's drainage has been pirated here from a southeastern course into Texas to become a southwest-draining tributary of the Pecos. The salient

known as "Taiban Mesa," north of the gap, shows somewhat less than 100 feet of Ogallala overlying Triassic red beds in the cliff. A coarse conglomeratic member of the Ogallala, marked by channel unconformities, possesses limestone cobbles up to 12 inches in maximum dimensions. The nearest source appears to have been the Permian Chupadera formation, 60 miles to the west. The scarcity of quartzose pebbles also seems to indicate a dominant stream from the high country about Vaughn, west of the present Pecos Valley.

The Taiban Mesa summit is caliche-capped. Scattered siliceous pebbles in this caliche lie 400 feet or more above the bottom of the arroyo in the gap. They also occur in a white sand immediately beneath the caliche.

Ogallala sediments are similarly exposed in the arroyo bottom near Tolar, for the high and low points of the modern topography here coincide roughly with those buried by the Ogallala formation. Quartzose pebbles in stratiform arrangement show in the arroyo banks.

Gravelly waste, carried by the arroyo in flood, has been derived in large part from the eastern slopes of the mesa. In this waste, pebbles of igneous and metamorphic rock are common. An earlier alluvium overlies the lower Ogallala slopes, so closely resembling the Ogallala itself that the disconformity is almost essential for separating the two. Some strata in this alluvium contain rehandled siliceous pebbles.

OGALLALA AND RELATED GRAVELS WEST OF PECOS RIVER NORTH OF CARLSBAD

Thirteen separate areas covered by the Ogallala formation and lying west of the Llano are shown on the geological map of New Mexico (Darton, compiled, 1928), the westernmost of these areas lapping up onto the Pedernal Hills almost to the Pecos–Rio Grande divide (fig. 1). This tract reaches an altitude about 2,000 feet higher than the northwestern and highest part of the Llano, 80 miles to the east. Thus a gradient of only 25 feet to the mile would be necessary to connect this near-divide remnant with the Llano.

The authors have found the quartzose pebbles on the surface or embedded in caliche at five different localities on the four of these thirteen areas which they have traversed. In addition, they have found pebbles and gravel *in situ* in more than a dozen localities in the gaps among these Ogallala remnants, where the state geological map shows only Triassic or Permian rock. The highest are along U.S. Highway 60, west of Vaughn, 1,000–1,200 feet higher than the Llano and 75 miles distant by a route directly across the region's contour lines (fig. 1). The gradient of the connecting line in this case is about 15 feet to the mile.

The best showing of gravel *in situ* was found along the private road to K.E. Ranch, 2 miles northwest of Ramon (locality 7, fig. 1). A large pit has exposed 35 feet of well-stratified, sorted, and worn limestone gravel with a liberal admixture of quartzose pebbles. Compared with silicate and silica pebbles near Negra and Lucy, both close to the crystalline Pedernal Hills (fig. 1), these siliceous pebbles near Ramon indicate another source area and something more than a 50-mile trip from parent-rock. The gravel is sufficiently cemented to maintain vertical pit walls, but the induration is inadequate for ledge-making on the slopes where the deposit occurs. Fifty miles to the east along the regional slope and not much more than 200 feet lower is the Llano scarp summit. This descent is too low to accept as an original gradient of the Ogallala formation across the Pecos Val-

ley. It can be increased to adequate proportions by considering the K.E. Ranch gravel as basal Ogallala and adding 500 feet to reach the original surface. But, because the average thickness of the formation in the Llano is reported to be from 200 to 300 feet and the depth of the K.E. Ranch deposit is not known, any picture of an adequate eastward-descending depositional slope seems improbable.

Limestone gravels with rare quartzose pebbles occur at lower elevations on dissected uplands at about the level of the Diamond A plain north and west of Hope (fig. 1). These gravels were believed by Fiedler and Nye (1933, pp. 38–39) to be younger than the "quartzose conglomerate" but were considered correlative by Morgan (1938, pp. 14–15). Their physiographic position and a thick caliche caprock indicate considerable antiquity, and it is not unreasonable to consider them as remnants of a local facies of the quartzose conglomerate-Ogallala fill.

OGALLALA AND RELATED GRAVELS IN THE CARLSBAD BASIN

The Pecos Valley from Roswell to the Texas line may be divided into two sections, the Roswell artesian basin to the north, floored with Quaternary valley gravels lying on the Chalk Bluffs and San Andres formations and structurally separated from a southern Carlsbad Basin section, which has an incomplete Quaternary gravel cover on the Rustler and Castile formations. Both sections have outcrops and well penetrations of the quartzose conglomerate, an indurated gravel, sand, and silt deposit beneath the younger and largely unindurated terrace gravels but above the Permian formations (pl. 1, *A*). This conglomerate has hitherto been considered an early Quaternary valley deposit in a post-Ogallala Pecos Valley (Meinzer, Renick, and Bryan, 1927, pp. 9–10; Fiedler and Nye, 1932, pp. 35–38; Morgan, 1938, pp. 14–15). Field evidence presented herewith inclines the authors to the interpretation of this conglomerate as basal Ogallala.

If the base of the quartzose conglomerate, penetrated by numerous wells in the Roswell (Morgan and Sayre, 1942, pp. 33–35) and Carlsbad basins,[3] is considered the base of the Ogallala and if it be assumed that no postconglomerate deformation has occurred, a former Ogallala fill of more than 1,300 feet along the Pecos depression is indicated.

In the Roswell Basin, earlier students have found the quartzose conglomerate cropping out in two localities at the north end, along two tributary streams from the west, and in the narrows at the south end where the Pecos crosses the Seven Rivers–McMillan escarpment (fig. 1). All outcrops are relatively low in the valley. Since the artesian basin has been so thoroughly studied, the authors made no attempt to find other outcrops of the conglomerate in it.

Lithologically, texturally, and in its sedimentary structures the quartzose conglomerate is identical with certain coarser phases of the Ogallala. Neither deposit, within the Pecos drainage, has yielded paleontological evidence of its age. Warned by the close similarity between original and re-worked Ogallala, the authors do not stress the resemblance as evidence of identity. The best evidence supporting their idea lies in the southern section and chiefly above the level of the valley terraces.

In this southern section is a triangular area of hilly land on Rustler and Castile rocks, south of the Black River and west

[3] Well records provided by H. P. Burleigh, U.S. Bureau of Reclamation, Carlsbad, 1947.

of the Pecos (fig. 1). Well-worn pebbles of durable siliceous rocks are widely scattered over it. They have been found most commonly on summits and higher slopes, where the originally associated, more readily weathered material has been removed. They range up to 950 feet higher than the junction of the Black and Pecos rivers, and 300 to perhaps 600 feet higher than the surface of the Llano plain to the east (fig. 1). This wide horizontal and vertical distribution has only one logical explanation: the entire triangular area has had a cover of Ogallala, and the contributing streams were not limited to drainage off the limestone Guadalupes to the west. That explanation becomes an almost inescapable conclusion when three hillside and hilltop remnants of conglomerate *in situ* are considered.

The highest part of the triangular area, the Yeso Hills, lies well south along the western edge, close to the Black River and some 200 feet higher. High on the northern slope are exposures of a limestone conglomerate, 150 feet above the river (locality 35, fig. 1; center sec. 12, T. 26 S., R. 24 E.; Carlsbad Caverns East quadrangle). It is far too high for terrace gravel, most of it is well indurated, and the exposures suggest that it is tilted. Its pebbles are well rounded and apparently record a longer trip than the 7 miles separating it from the Capitan reef scarp. Three quartzite pebbles were found in weathered waste of this conglomerate—a small number but difficult to explain except as derived from the indurated gravel.[4]

A low hill, 5½ miles directly west of the Pecos River and 200 feet higher, consists wholly of conglomerate (locality 36, fig. 1; corner of secs. 4, 5, 8, and 9, T. 26 S., R. 28 E.; Malaga quadrangle). The hill rises some 30 feet above the gently sloping plain surrounding it. Corroded limestone pebbles constitute 99 per cent of the surface waste, but the polished, brightly colored, siliceous pebbles are easily found. The surrounding plain is also sprinkled with them. The hill is nearly 300 feet lower than the Llano plain about 35 miles distant, but, being 100 feet higher than the highest river-terrace gravels, it appears satisfactorily explained as a remnant of a former Ogallala cover.

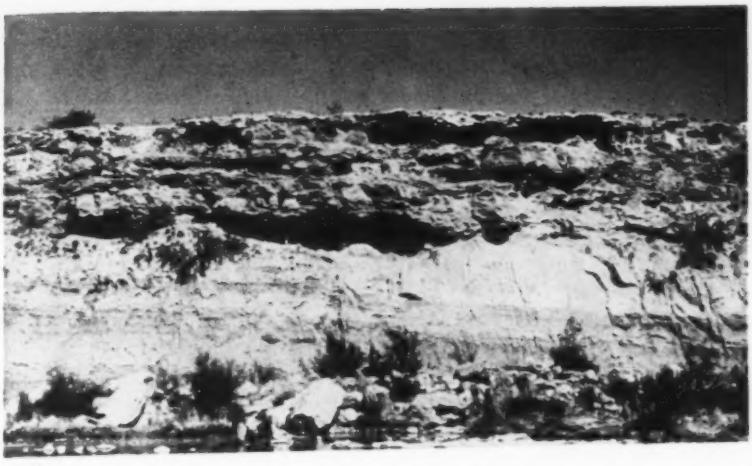
A mile and a quarter directly south of the Roy Forehand Ranch (locality 29, fig. 1; Malaga quadrangle) is an isolated hill composed mostly of Permian rock but possessing an abundance of siliceous pebbles and some of lava in its surface waste and ledges of limestone conglomerate with foreign pebbles on the summit. The hilltop is less than 1 mile from the Black River, but 150 feet higher. The river has cut a little gorge in the quartzose conglomerate at the ranch, 175 feet below the hilltop. The rock in the valley bottom and on the hilltop is so similar in every way that little imagination and

[4] The conglomerate differs lithologically from the Cretaceous sandstone and fossiliferous limestone remnants which Lang (1933) found about 3 miles to the north and interpreted as debris let down into a solution cavity in once overlying strata. Cretaceous fossils in float and patches of possible Cretaceous sandstone in place in the Guadalupe Range have also been reported by King (1942, p. 640).

PLATE 1

A, Angular unconformity between quartzose conglomerate and underlying Permian red beds along Pecos River, 4 miles north of Loving, N. M. (fig. 1; center S. ½, sec. 33, T. 22 S., R. 28 E.). Caliche caprock forms the ledge at the top of the conglomerate.

B, Quartzose conglomerate fills a solutionally enlarged joint in Capitan limestone near the crest of the Guadalupe Range north of Slaughter Canyon (locality 33, fig. 1; center N. ½, sec. 4, T. 25 S., R. 23 E.).



A

B

Occurrence of caliche

still less daring are required to see in this locality a record of a once-continuous indurated limestone conglomerate from channel floor to summit ledges (fig. 2), a former river gravel supplied largely from the western uplands but containing contributions from the Rocky Mountains, more than 200 miles to the north.

Were there only the hilltop conglomerate ledges, one who accepts preceding interpretations would be inclined to consider it a remnant of basal Ogallala. Were there only the river exposures, one familiar with the quartzose conglomerate along Black and Pecos rivers would unhesitatingly identify it as that deposit. most strongly to the authors is that the quartzose conglomerate was deposited before a Black River Valley existed.

From Herradura Bend southward, the Pecos River loses its broad lowland floodplain and, thence to Texas, traverses several narrow stretches with quartzose conglomerate and Permian red sandstone bluffs. One bluff at Herradura Bend (locality 26, fig. 1; Carlsbad quadrangle) is 60 feet high and composed entirely of the conglomerate formation, as is also the channel floor. The opposite bluff is only half as high because the river for a short distance here flows along the slope of a former hill of the conglomerate

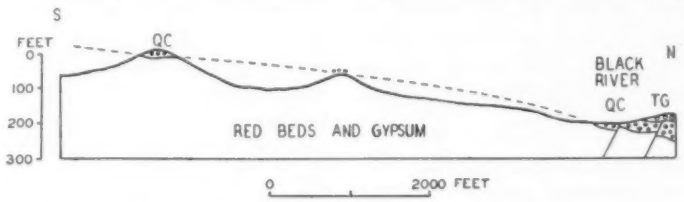


FIG. 2.—Relations of siliceous gravel residuals to the quartzose conglomerate near Forehand Ranch (Maluga quadrangle, New Mexico). *QC*, quartzose conglomerate and siliceous residuals; *TG*, terrace gravel.

The authors are strongly inclined to think that the two exposures are but parts of the same formation.

Blue Spring (locality 29, fig. 1; Carlsbad Caverns East quadrangle), although below terrace levels of Black River Valley, is a large ground-water discharge from Permian limestone and/or quartzose conglomerate, both of which crop out in the low hills constituting the spring alcove. The conglomerate here, 1½ miles from the river, lies more than 100 feet above it and has the same altitude as that on top of the Forehand hill, less than 5 miles away.

The foreign pebbles of both Forehand outcrops and of Blue Spring ledges came down along the Pecos from the north. How did they get 15 miles *up* the Black River Valley? The explanation appealing that later became buried in younger terrace gravels from which the Pecos has been superimposed. The upper 10–30 feet of the hill still stands above those younger gravels. A clean section at the crossing of U.S. Highway 31, ½ mile below Harroun Dam, shows Permian red beds in the river channel, overlain by 10 feet of red sandstone containing quartzose pebbles and that by 20 feet of gray lime-cemented conglomerate, also with abundant foreign pebbles (locality 27, fig. 1).

This is as low as any exposure of the quartzose conglomerate seen during this study, more than 400 feet lower than the outcrops at Blue Spring, 16 miles distant up Black River Valley. Pecos and Black River courses between the two localities afford many exposures, spaced close

enough to carry conviction that the formation is continuous. To bring the foreign pebbles to Blue Spring, the region must have been a uniform plain of fluviatile deposition, in the aggradation of which Rocky Mountain water participated. The constrictions imposed by present valley ways and the direction of flow determined by present gradients did not exist when the quartzose conglomerate was deposited. The flat top of the hill south of Herradura Bend is not a depositional surface. Assuming that no postconglomerate local warping or downfaulting has occurred, this flat hilltop is 350 feet below the level required to carry the siliceous pebbles to the deposit at Blue Spring. To reach up to the projected level of the Llano plain across this locality, the former Ogallala fill here must have been 600 feet thick.

OGALLALA RESIDUALS IN THE GUADALUPE RANGE

In five different places, worn quartzose pebbles have been found on the top of the pronounced Capitan Reef scarp, by which the mountains break off to the Black River lowland (fig. 1). A few were picked up on the summit just south of Jurnigan Canyon (locality 30, fig. 1; Carlsbad quadrangle), a large number lie from $\frac{1}{4}$ to $\frac{1}{2}$ mile east of the entrance to Carlsbad Caverns (locality 31, fig. 1; Carlsbad Caverns East quadrangle), and a few were found on the upland, 3 miles southwest of the cavern entrance. At all these places the pebbles lie essentially on bare rock surfaces and have no associated limestone pebbles.

The other reef-summit localities are on either side of the deep notch of Slaughter Canyon in the scarp near the heads of two minor canyons, Nuevo (locality 33, fig. 1) and Yucca[5] (locality 34, fig. 1; Carlsbad Caverns West quadrangle). At each, the quartzose pebbles occur in remnants of an indurated gravel and sandstone filling in opened joints and solution cavities of the Carlsbad and Capitan limestones (pl. 1, *B*), as well as scattered over the bare surface or throughout the thin soil. The display of thousands of these red and yellow polished pebbles on the mesa summit at the head of Nuevo Canyon is spectacular. More than 50 per cent of all pebbles in the sandstone and conglomerate here are siliceous.

Possible Ogallala residuals, consisting of foreign pebbles of schist and chert, have been reported[6] from Ares Peak (Texas Hill quadrangle) at an elevation of 5,782 feet A.T., in the central part of the Guadalupe Range. This is 16 miles north-northwest of the Nuevo Canyon locality and about 260 feet higher. It is 240 feet lower than the pebbles at the head of Yucca Canyon.

The pebbles of the Jurnigan Canyon locality lie 750 feet above the Harroun Dam exposure of quartzose conglomerate in almost the same latitude. The residual pebbles east of the cavern entrance lie about 1,100 feet higher than the conglomerate at Blue Spring, almost directly east. Those lying 3 miles southwest of the cavern are about 1,400 feet higher than the outcrop at the spring. The pebbles and conglomerate *in situ* at the Nuevo Canyon locality are 1,600 feet higher than those on the Yeso Hills, only 8 miles distant to the southeast and the highest found in the before-mentioned triangular area. At the Yucca Canyon locality they are 2,000 feet higher than in the Yeso Hills.

These siliceous pebbles on the summit

[5] The authors did not see this locality. It was discovered and reported to them by Bennett Gale, park naturalist, after the close of the field season.

[6] Carl Branson, personal communication.

of the reef scarp are considered to be Ogallala residuals and certainly are Rocky Mountain contributions. There was, by this view, a continuous southward and southwestward downgrade to the Ogallala alluvial plain along the foot of the Guadalupes, and the concept of an Ogallala bajada sloping eastward from them to the Llano (Sellards, 1933, p. 770) is incorrect. The Capitan Reef scarp is believed to be a product of pre-Ogallala erosion and to have been buried in the mounting waste toward the close of this Pliocene aggradation.

The scarp at the Yucca Canyon locality is nearly 1,500 feet high, and the younger gravel at its base slopes down another 700 feet to the approximate level of quartzose conglomerate outcrops near by in Black River Valley. Either the Ogallala formation in front of the scarp was 2,200 feet thick, or subsequent solution-collapse or warping has occurred to alter original levels. Warping along the line of the scarp seems supported by a comparison of altitudes of Ogallala remnants and residuals north of Roswell and west of the Pecos with the Yucca Canyon residuals and remnants. From Vaughn southward to Yucca by valley routes is about 200 miles, yet the descent, as read from the lingering quartzose pebbles, is only 100 feet. A gradient of 12 feet to the mile is secured by considering the Vaughn gravel as basal and equivalent to that along Black River, 2,200 feet below the Yucca remnants. But excessive thicknesses and improbably low gradients may be avoided by accepting some post-Ogallala uplift of the reef scarp relative to the adjacent lowland. This could be related to known Pleistocene movements of the Guadalupe block which faulted older alluvium along the west front of the range (King and Fountain, 1944). Differential uplift in this part of the scarp also seems required if the pronounced flatness of the top of the reef here is referred to the summit peneplain. The northwestward slope of this flat between Yucca and Nuevo localities is 100 feet to the mile.

Nevertheless, if the quartzose conglomerate is Ogallala, the thickest part of this formation lay along the present course of Pecos Valley, and this requires the concept of a pre-Ogallala Pecos Valley. The idea is not difficult to accept, for the valley lies along the strike and over the edges of the highly soluble evaporites of the Rustler and Castile formations. Sinks are actively growing today along this belt or are so recent that waste from their steep cliffs has not yet filled them. Also, most exposures of valley-bottom quartzose conglomerate show fracturing and strong tilting of big blocks because of solution-subsidence. Lee's idea (1925) that the course of the modern Pecos has been established by coalescence of sinks along the belt of upper Permian evaporites needs to be used also in interpreting the pre-Ogallala topography.

The induration of the quartzose conglomerate equals anything seen in the Llano gravels and far exceeds that of the overlying valley-terrace gravels. Generally, the matrix is as firm as the included limestone fragments, and the pebbles are impossible to crack out entire. Even river abrasion produces a smooth transection across matrix and pebbles. This cementation is not alone a matter of age; it implies also an original deeper burial than the terrace gravels have ever provided.

PEBBLE COUNTS

Pebble counts of the unweathered gravels (table 1) indicate the variable composition of the deposits. The gravels from the Ogallala formation and possible

Ogallala remnants show a dominance of limestone (38.6–60.3 per cent) compared with the quartzose conglomerate (2.0–11.5 per cent), which is composed largely of siliceous pebbles. However, all the quartzose conglomerate samples are from the axial portion of the Pecos Valley, and there are much higher limestone percentages in its remnants along the western margin of the basin. Exposures of the conglomerate along Black River, which are continuous with those along the Pecos, show overwhelming dominance of limestones. It seems just as probable that the concentration of siliceous material was brought about by an early valley phase of Ogallala deposition as by later Pleistocene re-working of Ogallala gravels.

Siliceous pebble percentages from Ogallala and related gravels and from the quartzose conglomerate are given in table 2 and shown graphically in figure 1. Again wide variability is indicated, but with close similarities in adjoining deposits, i.e., localities 7, 8, and 9 near Ramon and localities 31, 32, and 33 near Carlsbad Caverns (fig. 1). Three widely separated samples from quartzose conglomerate along the Pecos Valley axis (localities 12, 17, and 25) are strikingly comparable. The gravels from the Llano and the Mescalero plain differ from place to place. In general, there appear to be higher percentages of chert and jasper in all the deposits in the southern half of the region, probably because of proximity to Permian and older limestones in the Sacramento and Guadalupe mountains to the west.

TABLE 1

TOTAL PEBBLE PERCENTAGES OF UNWEATHERED OGALLALA AND OGALLALA (?) GRAVELS AND QUARTZOSE CONGLOMERATE

TYPE OF PEBBLE	LOCALITY (FIG. 1)							
	Ogallala ahd Ogallala (?)					Quartzose Conglomerate		
	1	2	4	7	11	12	17	25
Quartz	6.4	6.5	18.3	5.1	2.4	28.0	37.5	45.4
Jasper	1.7	.....	.....	.....	3.4	28.7	15.9	12.6
Quartzite	11.5	16.9	6.8	29.1	20.3	8.0	18.2	11.5
Chert	3.8	3.4	23.5	6.1	9.1	29.3	19.3	18.6
Granitic	14.1	22.8	7.8	6.8	10.1	3.3	6.8	0.5
Basic	0.8	0.7	.....	2.8	13.0	0.7	.....	.....
Limestone	60.3	46.2	42.9	43.0	38.6	2.0	2.3	11.5
Sandstone	1.2	3.4	0.5	7.1	2.9	.....	.....	.....

CONCLUSIONS

1. The relations of gravel remnants in the region to the Ogallala formation indicate that the Ogallala cover once extended south at least to the Texas line and covered all but the highest portions of the Sacramento and Guadalupe ranges. This conclusion is based not on attempted correlation of all gravels in the region as Ogallala, because many, as on the Mescalero plain, are clearly reworked, but on their occurrence in physiographic positions and at elevations which preclude re-working from an eastward-retreating Llano scarp. Remnants on the Sacramento plain and the

Guadalupe upland are at elevations accordant with or above the High Plains surface; those on the Diamond A plain and the upland south of Black River are on surfaces which slope eastward to the Pecos and, if re-worked, must have been derived from Ogallala deposits once present to the west rather than to the north or east.

TABLE 2

SILICEOUS PEBBLE PERCENTAGES FROM OGALLALA AND RELATED GRAVELS AND FROM QUARTZOSE CONGLOMERATE

Locality (Fig. 1)	Quartz	Quartzite	Jasper	Chert
1*	27.3	49.1	7.3	16.4
2*	24.4	62.8	.....	12.8
3	36.9	39.4	16.9	6.9
4	37.7	14.0	.....	48.4
5	49.1	21.8	3.6	25.5
6	48.3	26.3	6.3	19.1
7	12.5	72.5	.....	15.0
8	24.5	72.2	2.2	1.1
9	28.1	66.3	.....	5.6
11	6.9	57.5	9.6	26.0
12	29.8	30.5	31.2	8.5
13	72.2	2.2	7.2	18.3
14	60.7	0.5	8.2	30.6
15	54.2	.....	18.1	27.7
16	38.4	15.2	8.0	38.4
17	41.2	20.0	17.5	21.3
18	61.1	4.7	22.6	11.6
19	9.4	45.3	15.1	30.2
20A	54.2	18.4	6.8	20.5
20B	54.7	11.0	12.0	22.3
21	29.5	40.0	13.3	17.1
22	24.3	27.0	16.2	32.4
23	26.5	12.2	10.2	51.0
24	39.2	29.4	6.9	24.5
31	25.6	17.1	8.1	49.2
32	18.8	34.4	6.2	40.6
33	17.6	13.5	0.7	68.2

* Unweathered gravels with many crystallines.

2. The relations of the gravels to the quartzose conglomerate in the Carlsbad area, especially in the Black River drainage basin, indicate that a single deposit buried a land surface which was much like the present and had a relief of almost 3,000 feet. The occurrence of gravel remnants of similar lithology at all elevations between Pecos River levels and summits in the Guadalupe Range is the strongest evidence for this view.

3. It follows from the preceding conclusions that an ancestral Pecos depression, probably formed jointly by warping and solution-collapse, existed in pre-Ogallala time and that the present depression, enlarged by retreat of the Llano scarp and modified by later deformation and solution-subsidence, is in large part a resurrected feature. It also follows that the "Reef escarpment," which forms the southeastern margin of the Guadalupe Range, has been exhumed at least twice: first by stripping of weak Permian fore-reef deposits and later by removal of the Ogallala fill.

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CALICHE IN SOUTHEASTERN NEW MEXICO[1]

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ABSTRACT

Caliches with similar zonal profiles lie on the Pliocene Ogallala formation of the Llano Estacado and on three younger surfaces along the Pecos depression. Physiographic relations, the caliche profile, and other features indicate that the caliches were developed by soil-forming processes from parent-materials consisting largely of limestone gravels. The caliches and associated solution features provide a partial record of climatic changes since middle Pliocene time.

INTRODUCTION

TERMINOLOGY

Throughout the Southwest and the southern High Plains the term "caliche" is applied to calcareous caprocks, soil hardpans, and earthy or porous materials which occur at the surface or at shallow depths below the soil. Impurities are present in variable amounts, and siliceous and ferruginous materials may be associated. In other areas the term also has been used for aluminous, siliceous, ferruginous, and saline deposits; for sediments cemented and impregnated with calcium carbonate, i.e., mortar beds; and for incipient lime accumulations in the subsoil. This broad usage endangers the usefulness of the term, and it is desirable, if possible, to restrict the term to materials of calcareous composition (Sayre, 1937, p. 66), as indicated by the derivation of the word, and specifically to those calcareous materials which are formed in the zone of weathering. Subaqueous deposits, spring deposits, and mortar beds thus would be excluded.

The term "caprock" is used in this region to describe the uppermost zone of the caliche profile. It is a dense limestone only a few feet thick in most places, but topographically prominent because of greater resistance to erosion than the deeper zones have. Although it is a "layer" and may have bandings and horizontal partings that suggest minor strata, its outstanding structure is that of a self-breccia, recemented by massive sandy caliche and by additions of calcareous laminae which wrap around the fragments and occupy interstitial space of larger volume than that of the fragments. Thus the fragments commonly are completely isolated in the matrix. In the type of caprock herein denominated "Rock House," the brecciation is compounded to record two or more cycles of fragmentation and rehealing (pl. 1, *A*).

NATURE OF STUDY

The present study is based primarily on field observations made during a series of traverses across the Pecos depression and surrounding highlands over an area extending from the Texas boundary north to Santa Rosa, New Mexico (fig. 1). Additional observations were made of caliche in western Texas and southern Kansas. Selected specimens were examined in the laboratory, but a comprehensive study of them was not attempted.

The area is of particular interest in testing hypotheses for the origin of caliche because that material is extensively distributed on four different physio-

[1] Manuscript received May 6, 1949.

graphic surfaces and is derived from similar parent-materials, largely limestone gravels. The present paper describes the deposits and attempts to interpret their origin.

CLIMATE OF THE AREA

The area is semiarid with a mean annual temperature of about 52° F. and an average precipitation of 12–18 inches. Rainfall is greatest during July, August, and September and often occurs as heavy downpours with local thunderstorms. Evaporation is rapid as a result of low humidity and frequent high winds (Kincer, 1941).

GEOLOGIC AND PHYSIOGRAPHIC RELATIONS[2]

The Pecos Valley is a broad north-south depression bordered on the west by the Guadalupe and Sacramento mountains and on the east by the Llano Estacado of the High Plains. The mountains are composed largely of Permian and Pennsylvanian limestones, which dip gently eastward. Permian evaporites and Triassic red beds underlie Pleistocene and Recent deposits along the depression, and the Llano upland is underlain by sands and gravels of the Pliocene Ogallala formation (Darton, 1928*a*).

The High Plains of the Llano are believed to represent a constructional surface correlative with the Sacramento erosional plain in the Sacramento Range (Fiedler and Nye, 1932, p. 97). Lower erosion surfaces within the Pecos depression include, in descending order: the Diamond A–Mescalero plain, Blackdom plain, Orchard Park plain, and Lakewood terrace (fig. 1). Well-developed

[2] See accompanying papers by the same authors in this issue of the *Journal* for further details.

PLATE 1

A, Brecciated caprock composed of dense caliche fragments and siliceous pebbles (*A*), in a sandy caliche matrix ("Rock House" structure). The fragments show solutional modification and have a thin rim of manganese oxide. From caprock near Rock House, N.M. (fig. 1; Malaga quadrangle; NE. ¼, sec. 8, T. 26 S., R. 29 E.). Specimen is 8 inches long.

B, Concretionary mass of dense banded limestone in chalky caliche zone above Ogallala deposits. Western margin of the Llano Estacado at Maljamar, N.M., along N.M. Highway 83.

C, Banded travertine from concretionary mass similar to the above. Llano scarp along N.M. Highway 31, 12 miles north of Maljamar, N.M. Specimen is 3 inches long.

PLATE 2

A, Caliche zones: (*1*) dense, banded caprock above hammer; (*2*) brecciated caprock, prominent ledge below hammer; (*3–4*), chalky caliche with cupped pebbles below ledge; (*5*) limestone pebble gravel, the parent-material, at the base of cut (see fig. 3). Blackdom plain, 1 mile northeast of Hope, N.M. (fig. 1).

B, Cupped-pebble zone at above locality.

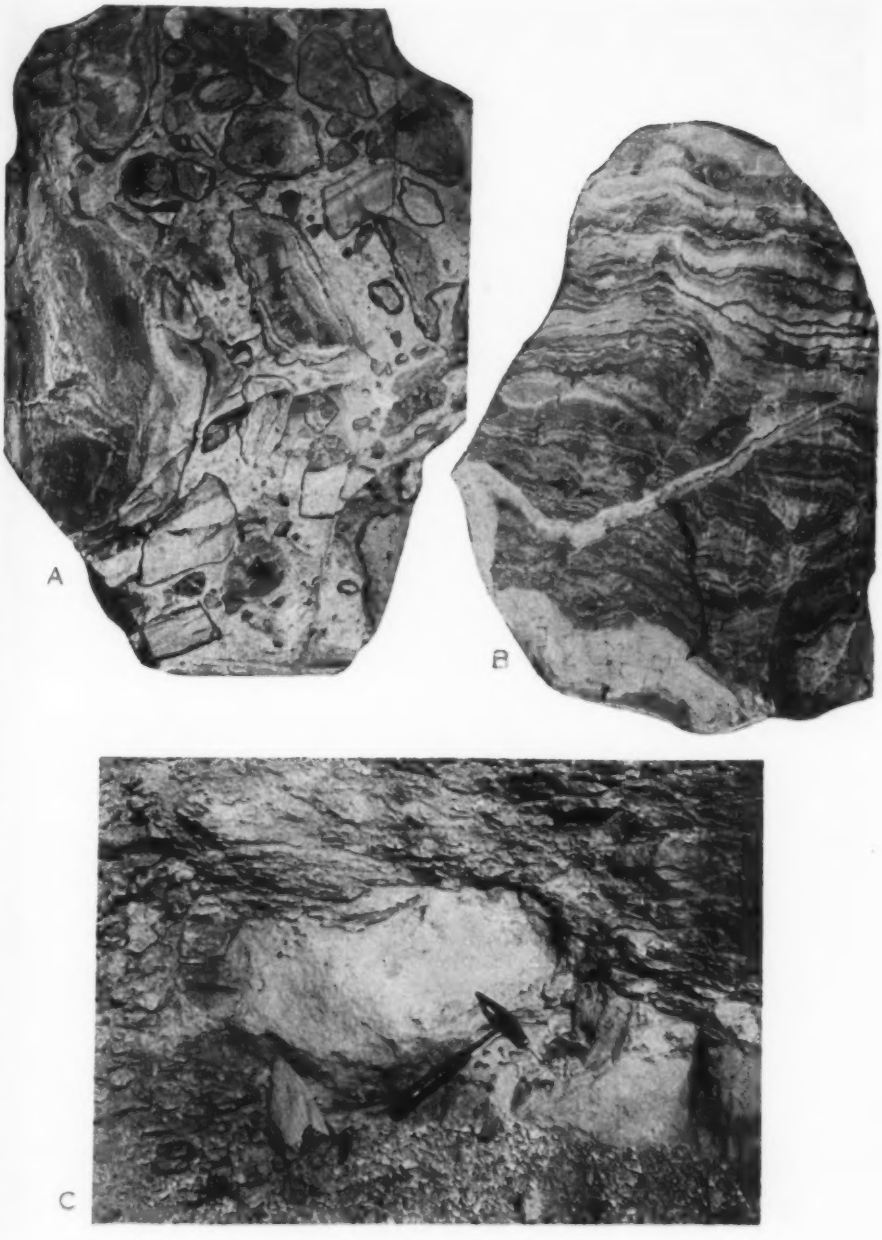
PLATE 3

A, cross section showing caliche crust on cupped limestone pebble; *B*, *C*, and *D*, upper surface of cupped limestone pebbles. From cupped-pebble zone in caliche pit, 1 mile northeast of Hope, N.M. The largest specimen is 3 inches long.

PLATE 4

A, Caliche fragment from surface rubble. A core of sandy caprock is surrounded by travertine bands. The present upper surface is outlined by solution, and undersurface has a recent crust of pustulose, spongy travertine. Hagerman Heights, ½ mile east of Carlsbad, N.M., along U.S. Highway 62. Specimen is 6 inches long.

B, Degraded, spongy caliche below sandy soil. Solution cavities are filled with soil and caliche fragments. Junction U.S. Highway 62 and N.M. Highway 31, 2 miles northwest of Tower Hill (fig. 1).



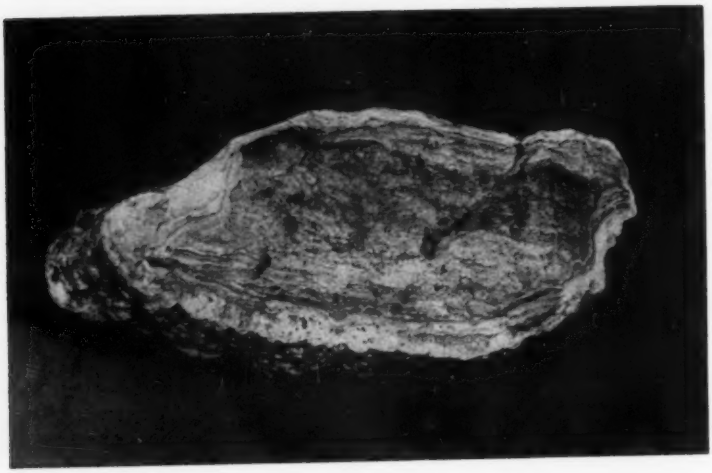
Brecciated caprock and concretionary structure

A

B

Caliche profile

Cupped caliche pebbles



A

B

Caprock with recent travertine crust; degraded caliche and solution features.

caliche lies on all these surfaces except the Lakewood terrace, and in places it is found on transition slopes as well.

Limestone gravel constitutes the parent-material of the caliche at essentially all localities, and either it is present in the section, or its former presence is recorded by siliceous residuals. The gravels on the Llano and the Sacramento plain are of Ogallala age, whereas those on younger surfaces were derived largely from the Ogallala and from limestones in the Guadalupe and Sacramento ranges and are of Pleistocene age. Deposits occupying local basins on the Mescalero plain belong to the Pleistocene Gatuna formation (Robinson and Lang, 1939, pp. 84–85), and extensive dune sands on this surface are termed "Mescalero sands" (Darton, 1928*b*, p. 59).

The physiographic and geologic relations clearly indicate that the caliche varies in age from place to place and cannot be used as a stratigraphic horizon marker.

THE CALICHE PROFILE

DESCRIPTION

The two localities found in 1946 which best show the weathering profile of caliche overlying limestone gravel are near Hope, in northwestern Eddy County, and near Mesa, in southwestern De Baca County. Because both are in gravel-pit walls and will become obscured after the pits are abandoned, several other localities with less complete sections will also be noted.

The Hope Sections.—Two pits lie near N.M. Highway 83 east of Hope, in sec. 20, T. 17 N., R. 23 E., and sec. 17, T. 17 N., R. 24 E., respectively (figs. 1 and 3). Both are excavated in a partially cemented gravel of the Blackdom terrace along the Rio Penasco. Both possess a laminated and brecciated caprock a foot or so thick, the brecciation and rehealing indicated as having occurred two or three times (pl. 1, *A*). Below the caprock is a weak, chalky caliche grading down in 3 or 4 feet into limestone gravel (pl. 2). Few entire pebbles are recognizable in this zone. Those that are identifiable as originally pebbles possess an extraordinary amount of solutional reduction of the upper part. Original outlines are retained only on the lower half to three-fourths of the pebble surfaces. Tops are truncated by roughened, flattish new surfaces, clearly the result of solutional attack by down-moving soil water (pl. 3). In a considerable percentage of them the solutionally made surface is concave upward, with a sharp little rim bounding the concavity. In a few such pebbles the concavity has a surviving central nubbin, surrounded by a moat. In places the ensemble looks remarkably like a mass of clam shells, with all concavities upward.

The matrix of this zone is chalky and friable, and many pebbles may be picked loose with the fingers. Weak cementation also characterizes the gravel below the zone of this solutional modification.

Nye (Fiedler and Nye, 1932, p. 34) reported the pebble-faceting in one of these pits as due to rain-water solution during aggradation while each layer of pebbles successively lay on the surface. Such rain-water modification of limestone pebbles lying on the surface is a widespread phenomenon in the Pecos Valley, but there are serious objections to this interpretation for the solutionally truncated pebbles of the Hope sections.

Nye's hypothesis requires an exceedingly slow accumulation. This he recognizes. But it also requires the following improbabilities: (1) The ancient stream deposit must have lain dry for intervals

of much more than a thousand years between the floodings that brought additional gravel; (2) each accretion of gravel was a layer only one pebble deep; (3) no overturning of already truncated and cupped pebbles ever occurred when a new layer was added.

Careful but fruitless search was made for an expectable relation, by Nye's hypothesis, of upper pebbles resting in the cups of immediately subjacent ones. Instead, several cases were found where a cavity lay immediately above a truncated pebble, the cavity arched over by laminated caliche matrix. In places where interstitial caliche rested directly on a pebble's truncated surface, it had a structure of short, close-set, vertical columns suggesting tiny stalactites and obviously was a deposit made in the cavity left by removal of the upper part of the pebble.

Although lamination is a common structure in the interstitial lime of this zone, it is limited largely to the lower sides of pebble remnants, and no case was found where laminated caliche was wrapped across the truncated upper surfaces.

It is concluded, therefore, that the 3-foot zone of altered pebbles is a weathering profile. Descending soil water has dissolved lime from the tops of pebbles during wet seasons or cycles. During succeeding dry spells, lingering films of this water, clinging to the bottoms of pebbles, deposited lime to make the laminated additions. The unaltered gravel beneath this zone may have lain below the water table while most of these changes were going on. Scattered entire pebbles of limestone found in the caprock must, by the writers' hypothesis, be later introductions.

A section in a large gravel pit along N.M. Highway 83 on the western outskirts of Artesia, 20 miles east of Hope, shows two different gravel deposits, both presumably post-Blackdom, separated by discontinuous red, laminated silt and clay. The top of the lower gravel has a thin layer of solution-truncated pebbles, both where covered by the silt and where the upper gravel rests directly on the lower. There is no accompanying calichification. Nye's explanation is perfectly appropriate here. A horizon of cupped pebbles in a gravel accumulation is a record of disconformity.

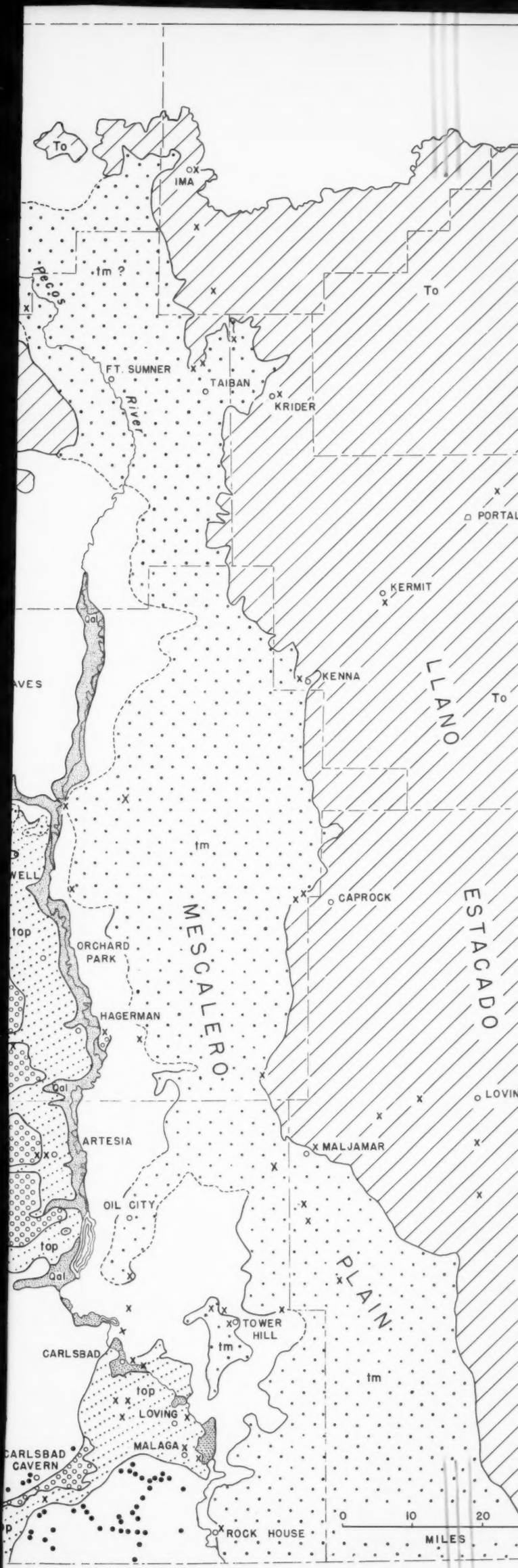
The Mesa section.—From Mesa to Vaughn, along N.M. Highway 285, the country rises from 4,500 to 6,000 feet A.T. through a series of erosional and sink-produced slopes which are not, like the Llano, remnants and records of a flat-topped depositional plain. Because, however, the slopes lie above the Blackdom level and carry many gravel residuals with siliceous pebbles, the fluvial materials are taken to be remnants of the Ogallala formation (Bretz and Horberg, 1949), and the surface is considered part of the Sacramento plain.

A large borrow pit for road material lies a little off the southwestern side of the highway, about 12 miles northwest of Mesa, at an altitude of about 4,700 feet, A.T. (figs. 1 and 2).[3] Being older than all terrace stages of Pecos Valley, it has expectably a more mature weathering profile (fig. 3). It does contain almost all the evidence necessary to prove that the caliche of southeastern New Mexico is the weathered product of limestone gravel.

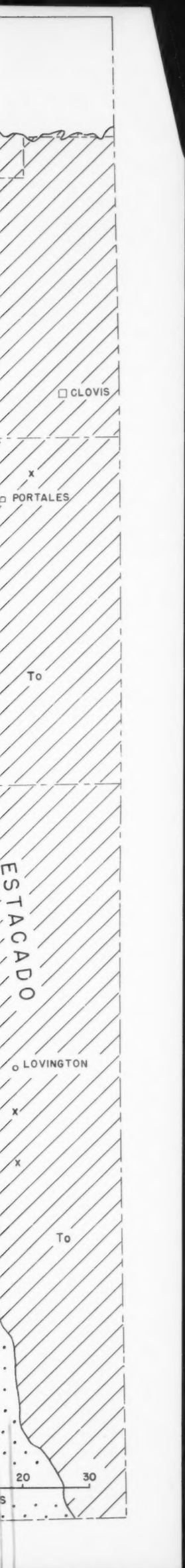
The upper 1 foot of the section afforded by this pit consists of dense, slabby, banded, and brecciated caprock, with strong salmon-pink color and beautiful concretionary bandings to the center of

[3] No more precise location has been obtainable.

FIG. 1.—Caliche localities and physiographic



physiographic features in southeastern New Mexico


CLOVIS
PORTALES
To
ESTACADO
LOVINGTON
To
20
30

the primary units of the breccia structure (zone 1, fig. 2). Below this are 2 feet of less indurated caliche with less well-shown banding and more prominent breccia structure (zone 2). Texturally, it is still "Rock House" caprock.

A gradation of about 6 inches downward reaches a zone of nodular, poorly indurated caliche, 4 feet thick (zone 3). The nodules can be picked out of the face of the cut with the fingers. Cracked open, they reveal very good concentric structures.

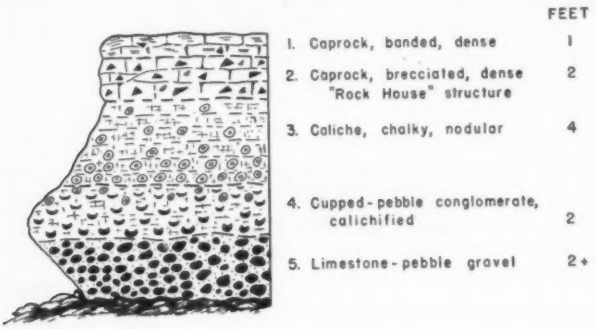

FEET
1. Caprock, banded, dense 1
2. Caprock, brecciated, dense "Rock House" structure 2
3. Caliche, chalky, nodular 4
4. Cupped-pebble conglomerate, calichified 2
5. Limestone-pebble gravel 2+

FIG. 2.—Zones in the caliche profile. Caliche pit on Sacramento plain, 12 miles northwest of Mesa, N.M. "Rock House" structure is a field term for the breccia, being named from caprock specimens from Rock House, N.M.

From 6 inches to 1 foot deeper, many of the nodules have a cup on the upper side.

At a total depth of 6–8 feet these cupped nodules consist of caliche layers only for their lower part. The smaller, upper part is a remnant of a limestone pebble!

A foot or so lower in the section, the remains of the limestone pebbles exceed in bulk the caliche part of the nodules (zone 4). The limestone is soft and weathered.

A little lower, pebbles take the place of nodules, all cupped on the upper side. The limestone is bright and unweathered in the center, and there is only an incipient caliche coating on the bottom. The lower 2 feet in the section consist of unweathered limestone-pebble gravel (zone 5).

Quartzose pebbles occur throughout the entire section.

The conclusion drawn from this section is that the entire sequence was once a limestone gravel with scattered siliceous constituents and is now a weathering profile showing greatest alteration at the top, where it has developed the typical caprock structure, a surface-weathering product of this region's climate on parent-material of limestone gravel. The gradation downward into nodular caliche suggests that primary units of the breccia caprock may owe their origin to such nodules. The gradation of nodules into pebbles indicates nodule origin from wastage of upper surfaces and accretionary growth on lower surfaces of original pebbles. Thus each nodule is a record of a former pebble. So complete is this transformation in the upper part of the nodule zone that many are concentric to the core. Others still enclose a remnant of the original limestone pebble or may hold a quartzose pebble. As nodule growth beneath a wasting pebble has progressed, it

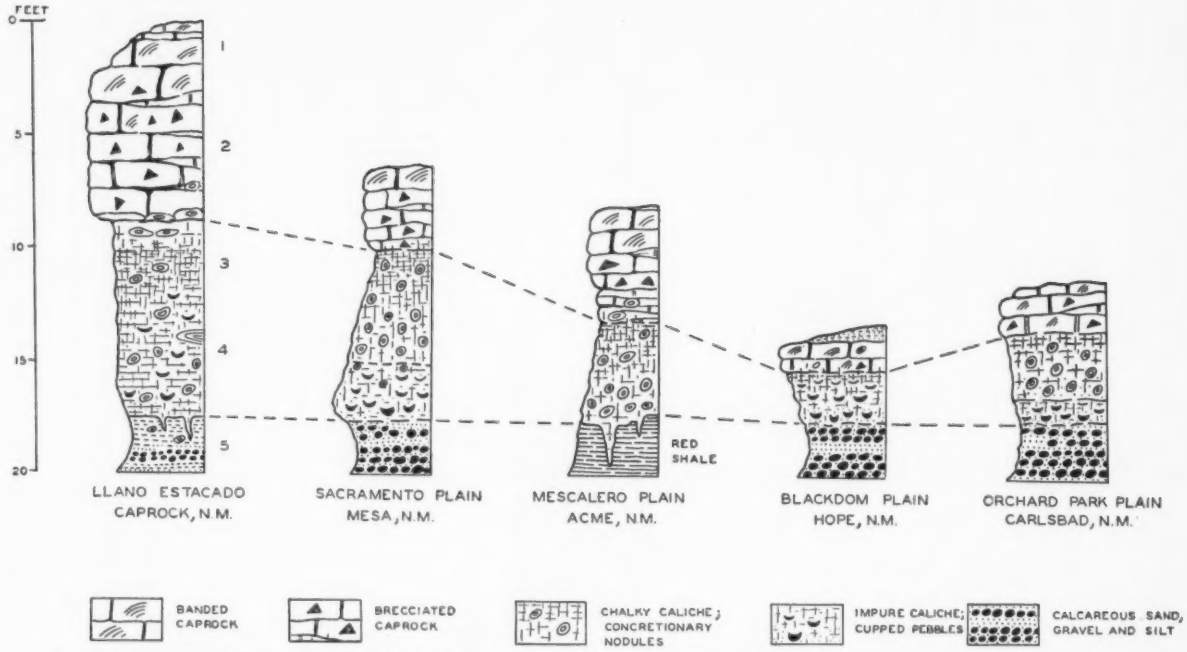


FIG. 3.—Variation in caliche profiles on surfaces of different ages. Llano scarp near Caprock, N.M., 1½ miles south of U.S. Highway 380; caliche pit about 12 miles northwest of Mesa along U.S. Highway 285; caliche pit, 2 miles southwest of Acme, N.M., along U.S. Highway 70 (23 miles northeast of Roswell, N.M.); caliche pit, 1 mile northeast of Hope, N.M.; cut along U.S. Highway 62 at Hagerman Heights Carlsbad, N.M.

has come to include small bits of other material, perhaps also concretionary in structure, perhaps quartzose.

The one difficulty with the writers' interpretation is that, where most of the nodules should show, in their cross sections, a series of diminishing, concave-upward saucer-forms toward the top, most of them show an equidimensional concentricity. Some, however, show the structure expectable by the genesis proposed.

A similar section, but with the cupped-pebble zone less well shown, is exposed in a caliche pit along the same highway, about 5 miles farther northwest.

Hagerman Heights section.—Just east of Pecos River at Carlsbad is a definite terrace known as "Hagerman Heights." It is considered a part of the Orchard Park surface (fig. 1). Grading for U.S. Highway 62 has made a long cut through the scarp of this terrace, and in the sides of this cut is an instructive section (fig. 3).

Caprock is wholly limited to the flat surface of the terrace. It averages 18 inches in thickness but locally is 4 feet thick. It possesses concentric banding of laminae around older caliche fragments and embedded quartzose pebbles. Manganese oxide "ink lines" are involved in this banding.

Below the caprock are 3–4 feet of rather loose, nodular, chalky, poorly indurated, and poorly layered caliche, with but few quartzose pebbles as compared with the caprock. Their relative abundance in the caprock can well be the result of concentration through solutional removal of associated calcareous pebbles.

This nodular caliche grades down into about a foot of gravel, in which many limestone pebbles have had their upper portion eaten away by solution *in situ*, leaving "half-shell" or cupped forms, comparable to those in the Hope and Mesa sections.

Below this zone is a 5-foot bed of cemented limestone gravel with pebbles entire and, below that, a brown stratified silt with incipient calcareous cementation.

Telltale Bluffs section—A cliff, continuous for a mile along the east side of Pecos River, about 2 miles southeast of Carlsbad, is called "Telltale Bluffs." The basal part of the cliff is of strongly tilted Permian limestone beds, above which are 50 feet or so of the "quartzose conglomerate" formation (Bretz and Horberg, 1949), composed chiefly of Permian and Triassic red-bed debris but with siliceous pebbles in every stratum. The amount of red-bed contribution decreases toward the top, giving way to a dominance of grayish, largely limestone conglomerate and lime sandstone. The upper 10 feet of this may be described as a nodular aggregate, and the top 3 feet or so are typical caprock, indurated enough to overhang the cliff brink for the entire mile of length. The summit of Telltale Bluffs lies in the Orchard Park niveau.

The caprock breaks into slabs along nearly horizontal planes. Quartzose pebbles are scattered throughout. The texture is fragmental, older pieces of the caprock being surrounded by concentric laminae and those concretionary units being embedded, although not in contact, in a dense caliche matrix. Where the original fragments were small, the effect is that of a rude pisolitic texture.

In the northern part of the bluff the nearly horizontally layered caprock overlies and truncates a 15° dip in the underlying conglomerate and sandstone. This disconformity is interpreted as a weathering profile superposed on the underlying highly calcareous conglomerate, and

the stratiform structure of the caprock is interpreted as developed *in situ* by this process rather than being true strata of successive deposition on the underlying tilted rocks.

Inconspicuous but consistently present, at depths of 8–10 feet, are cupped pebbles. Above their level is nodular caliche, below it the limestone pebbles are entire.

Another river-bluff section, about 1 mile south of Telltale, shows a feature seen in several places in caliche immediately subjacent to caprock. It is that of "eviscerated" pebbles, the solutional attack having first breached the upper surface and then having dissolved away much of the interior, leaving a hollow partial shell, which later has become filled with sandy material. This, however, may have occurred during aggradation of the deposit rather than during the later calichification.

Carlsbad airfield section.—A large roadside pit for highway material, excavated in gravel of the Orchard Park plain, lies across U.S. Highway 62 from the airfield, 2 miles south of Carlsbad. The caprock is the familiar caliche breccia, cemented by regrowth to a dense, slabby material. Below this are about 6 feet of nodular, chalky, punky caliche containing a few siliceous pebbles and some still recognizable limestone-pebble outlines.

Gradation from this nodular material down into firm limestone conglomerate with its pebbles entire is by an irregular zone of truncated pebbles, with numerous cupped forms.

Exposures between Lovington and Maljamar, Lea County.—West from Lovington, along N.M. Highway 83 to the Llano scarp overlooking the Mescalero plain, there are numerous shallow cuts and scrapings in the surface of the caprock, which show what is believed to be genetically a significant feature of the rock.

The Llano plain along this route is an almost flat surface, diversified only by a few broad, shallow sinks. Caliche caprock lies beneath a thin soil composed in part of wind-deposited material. Where exposed, the caprock is a dense limestone but is readily cracked and broken into slabs by road-making machinery. It parts along "bedding" planes and already existing vertical cracks. Rarely is any movement of slabs from position shown, except where disturbed by the grader.

Texturally, each of these slabs is a breccia aggregate. The internal arrangement of component parts shows no tendency whatever toward a stratification paralleling top and bottom of the slab. The structure of the fragments constituting the breccia shows that they have been derived from an older laminated porcellanous caliche.

The fragments are rarely in contact. They are characteristically surrounded by layers of later-deposited calcium carbonate. Some also possess thin rims of manganese dioxide. The matrix embedding the fragments is a sandy, fine-textured lime. The aggregate is so similar to that shown in plate 1, *A*, and figure 5, from Rock House, New Mexico, that, without proper labeling, even the collector would be at a loss to differentiate.

Before being disturbed by the grader, these slabs were already discrete units. They can be pried loose with a hammer. The upper surfaces of slabs are covered by porcellanous caliche, finely laminated parallel to that surface but with the laminae turning over the edges to descend vertically into bounding cracks. The bottoms of the slabs are characterized by a pustulose surface of added lime carbonate, commonly pinker in color

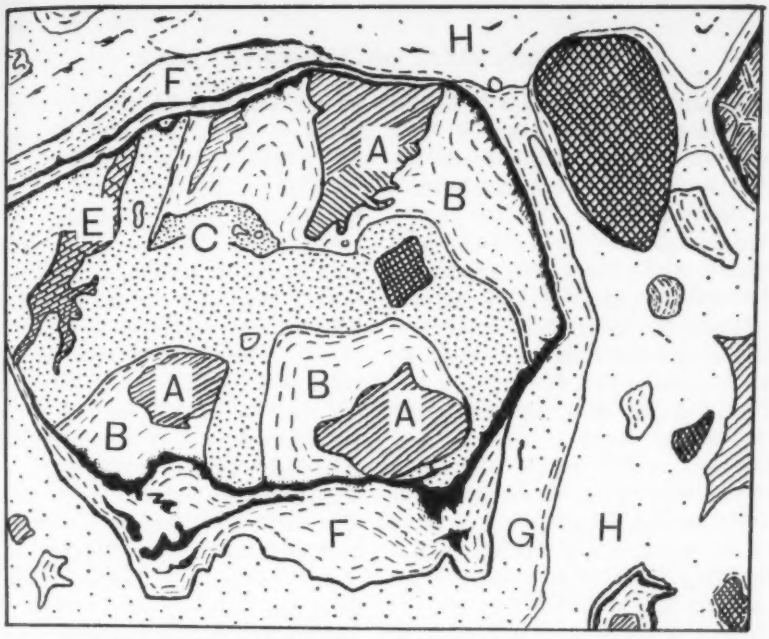


FIG. 4.—Polished surface of brecciated caprock from Rock House, N.M., showing several generations of fragments and matrix. *A*, crystalline travertine; *B*, sandy, banded travertine; *C*, sandy caliche; *D*, sandy matrix; *E*, travertine veinlet; F, banded travertine; *G* and *H*, sandy matrix. Siliceous pebbles are cross-hatched; manganese oxide rims are in solid black. Width of surface is 45 mm.

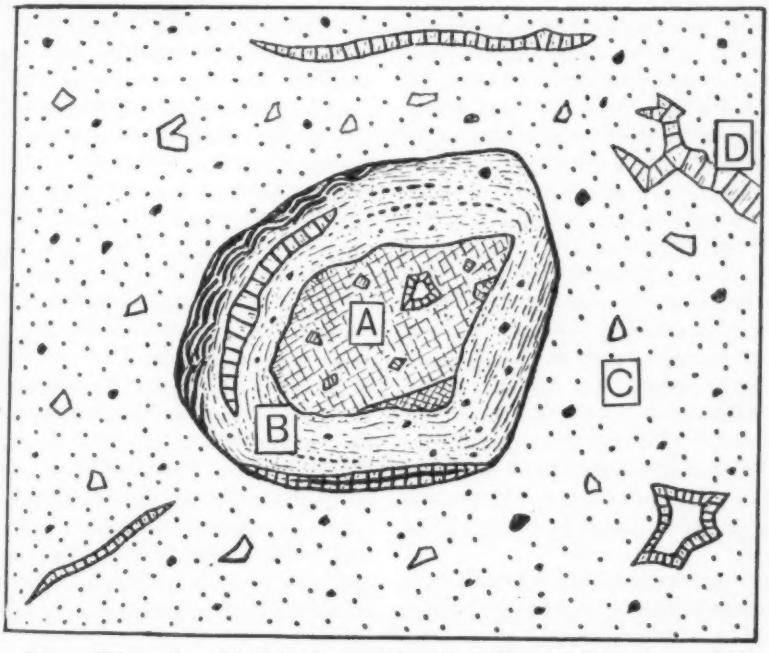


FIG. 5.—Thin section of brecciated caprock from Rock House, N.M. *A*, fine crystalline travertine; *B*, banded travertine; *C*, sandy matrix; *D*, coarse crystalline travertine veinlet. Manganese oxide rim in solid black. Width of section is 6 mm.

than the surface laminae but of just as dense and porcellanous material. This bottom addition does not share in the concentric wrapping of the slab. It truncates the lower edges of the laminae on the slab margins and appears to have no laminae in itself. Truncation appears to be due to development of solutional surfaces before deposition of the bottom crust. Solution markings are common on upper surfaces of the slabs.

Clearly, these slabs have been growing *in situ;* the pustulose underpart may still be growing. The writers believe that these additions to the slabby fragments of the brecciated caliche have taken place on the surface of the Llano, just under a thin, noncalcareous soil, through the agency of rain and soil water. The added material is believed to have come from wastage of once overlying portions of the original caliche, whose basal part now survives in the slab interiors.

Were these slabs to become more broken by weathering or by deposition in the cracks and the more nearly equidimensional pieces rotated and then recemented to become a continuous rock body again, another episode of brecciation would be added to the caprock's history. Such repeated cycles of brecciation, solutional wastage, and recementation by growth of laminar wrappings is strikingly recorded in the specimens from Rock House (pl. 1, *A;* and fig. 4).

Although showing only the very top of the caliche profile, these exposures west of Lovington are miles from any river bluff or terrace scarp, and they demonstrate that caprock antedates the declivities at whose summits it may crop out and therefore antedates the groundwater levels influenced by those declivities.

The profile of weathering below the caprock in this general area is revealed by sections at the Llano scarp near Maljamar. In a cut along N.M. Highway 83, 1 mile east of Maljamar, a thin remnant of the caprock is underlain by about 15 feet of chalky, porous caliche in rude layers, 1–3 inches thick, and contains lenticular masses, 2–6 feet in length, of dense brecciated caliche similar to the caprock (pl. 1, *B* and *C*). This grades downward into the parent-material—a brown, silty, calcareous sand of the Ogallala formation. A similar section is exposed along N.M. Highway 31, about 12 miles to the northwest, where 10 feet of dense, brecciated caprock are underlain by an equal thickness of chalky, concretionary caliche, which contains lenticular masses of dense caliche up to 6 feet in length. The underlying Ogallala formation is a fine, silty sand. A partial section of the Llano's weathering profile may be seen in a caliche pit along N.M. Highway 83, about 11 miles east of Maljamar, where the layered structure and lenticular masses in the chalky caliche zone are particularly well shown. Siliceous pebbles appear to be absent at all these localities. The sections differ from those previously described by the absence of a cupped-pebble zone and a well-defined nodular zone. This appears to be due to the fine-grained texture of the parent-material. The thicknesses of the caprock and chalky zone is greater than that on younger surfaces and typifies a mature stage of development.

Section near Caprock, Lea County.— Another mature caliche profile on fine-grained Ogallala sediments is exposed at the Llano scarp, about 5 miles southwest of Caprock (fig. 3). In this section the caprock reaches a thickness of about 30 feet and is composed of dense, massive, laminated, and brecciated caliche which contains relicts of nodular structures. It

grades downward into chalky, nodular caliche, which is about 10 feet thick and, like that near Maljamar, is rudely layered and contains dense, lenticular masses, 1–2 feet in length. Inconspicuous small chert nodules and stringers occur in the chalky caliche. The unaltered Ogallala deposits at the base of the section consist of sandy silts with pebble bands and calcareous nodules and veins. Siliceous pebbles occur throughout the section. Some of the nodules in the chalky zone resemble altered limestone pebbles, but definite identification was not possible. The abundance of nodules, however, suggests that limestone gravels were once present and were destroyed during calichification.

Section near Taiban.—A thin caliche profile developed on Ogallala sand is exposed at the Llano scarp, 3 miles north of Taiban, De Baca County, and is repeated along the scarp at localities to the east and southwest (fig. 1). The caprock is only 2–3 feet thick and has a chalky appearance. The underlying porous caliche, which is about 3 feet thick, is rudely layered and contains scattered nodules of dense brown travertine. This grades downward into a silty, calcareous sand, about 15 feet thick. There are calcareous veins and nodules in the upper part, and the lower 3–4 feet are cemented into a mass of nodular, concretionary vertical pipes. Underlying the sand is a coarse, poorly indurated conglomerate with boulders up to 14 inches in diameter. Although the thinness of the profile, as compared with other Llano sections, may be due in large part to removal of the caprock by erosion, it is also possible that it reflects a lower calcium carbonate content in the parent-material.

Yeso section.—A caliche section on an outlier of the Llano plain west of the Pecos is exposed in a pit along the north side of U.S. Highway 60, 7 miles northwest of Yeso, De Baca County (fig. 1). At this locality a dense, brecciated, and laminated caprock, 3 feet thick, overlies about 5 feet of soft, nodular, rudely layered caliche. This, in turn, rests on and penetrates downward into brecciated Triassic red beds without intervening Ogallala sediments. Siliceous pebbles in the caliche, however, indicate that Ogallala gravels were once present. Nodules and fragments in the soft caliche zone are composed of dense salmon-colored travertine similar to the caprock, and many are solution-faceted and encrusted with secondary caliche. These relations suggest a second-cycle profile in which earlier caprock formed the parent-material. It is probable that this process was continuous during lowering of the surface and that the original parent calcareous sand and gravel may have lain well above the bedrock now being intruded by caliche.

Acme section.—Another second-cycle profile is shown in a caliche pit along U.S. Highway 70, about 22 miles northeast of Roswell (2 miles southwest of Acme, Chaves County) (fig. 3). The caliche in this area forms the surface of the Mescalero plain, and east of Acme it is covered by Mescalero dune sands, which are probably of Pleistocene age. The section consists of dense, laminated, and brecciated caprock, 3 feet thick, underlain by 6 feet of soft nodular caliche, which overlies and penetrates downward as caliche roots into Triassic red beds. Siliceous pebbles are present in the caliche. The nodules are composed of dense travertine and are encrusted with layers of softer caliche.

CONCLUSIONS REGARDING THE CALICHE PROFILE

The weathering profile in the calcareous gravels of the Ogallala formation of

the Llano and three successively younger and lower surfaces between the Llano and the mountains to the west consistently possesses a caprock of (1) laminated caliche and (2) firmly cemented caliche breccia; (3) a subjacent zone of crumbly, nodular, chalky caliche with no pebble outlines, below which there is gradation by (4) a zone of cupped pebbles into (5) limestone gravel unaltered except by cementation (fig. 2). Exposures vary; but, if deep and clean enough, one may expect to find evidence for these alteration units wherever calichification has occurred on a limestone gravel in the region.

Except close to the Guadalupe and Sacramento limestone ranges, whence came the abundant calcareous gravel of the Ogallala formation, one may anticipate finding scattered siliceous pebbles in all four altered units, as also in the deeper unaltered gravel. Their occurrence in the brecciated caprock was as much a puzzle during the early weeks of the field study as was the compounded breccia itself. It is confidently asserted that they will remain an unsolved puzzle for anyone who refuses the explanation here advanced.

A comparison of caliche profiles on surfaces of different ages (fig. 3) shows that there is a general increase in the depth of the profile with age. There appear to be many exceptions, however, as indicated by the Taiban section, which is abnormally shallow, and the section at Hagerman Heights near Carlsbad, which is abnormally deep. Many additional measurements would be needed to establish this general relation on a quantitative basis.

Age is but one factor in determining the depth of the weathering profile. Topographic setting, rainfall, erosional attack by wind and water, temporary burial by eolian sand, and the composition and texture of the parent-material—all these and perhaps other factors have functioned. But downward migration of the bottom of the nodular zone as pebbles have been consumed has been continuous, and the front of this advance has been marked by the zone of cupped pebbles. The Hope and Mesa sections provide a detailed record of the transitional stages between limestone gravel and nodular caliche.

In the compound breccias of the caprock is the record of climatic oscillations, alternating between pluvial and semiarid during the history of the calichification.

In the laminae locking the breccia fragments together is the record of solutional wastage and disappearance of somewhat higher levels of the original calcareous gravel or sand deposit.

Where caliche overlies noncalcareous red beds, the writers are persuaded that the original characters of an original limestone gravel or sand have all been destroyed in calichification.

Caliche on marine limestone bedrock has been found only in proximity to a calichified limestone gravel on this bedrock and appears to record the thin edge of that gravel cover when the alteration took place. A proper climatic environment and a calcareous substratum do not seem to encompass all the requirements for caliche-making. The abundant interstices of sand and gravel appear to be necessary, also.

LITHOLOGIC DESCRIPTION

POLISHED SURFACES AND THIN SECTIONS

Caprock.—Microscope studies show that the varying textures in both banded and brecciated caprock are due to differences in (1) amounts of detrital impurities, (2) crystal grain size of the caliche,

and (3) manganese and iron oxide colorations. Although a sharp boundary cannot be drawn between the two caprock zones, the upper banded caprock is more massive and crystalline and has fewer impurities.

The characteristic texture of the caprock is best displayed in the brecciated zone and consists of unoriented fragments of caliche in a sandy limestone matrix (pl. 1, *A;* fig. 4). Individual fragments are composed of banded crystalline travertine, older sandy matrix, concretionary nodules, siliceous residuals, or masses of older breccia. In places there is evidence of partial replacement of fragments by the matrix. Several generations of breccia are shown. Many of the fragments are surrounded by layers of concentrically banded travertine and are rimmed by an impure black manganese oxide glaze. The glaze defines the fragments as sharply as if they were outlined in ink and is one of the most striking features of the rock. It margins solutional surfaces and penetrates irregularly into the fragments. Chemical analyses of the glaze show a concentration of manganese oxide, but no higher percentages of iron oxide than are present in the associated caliche.

As far as determinable, the carbonate in the caprock is calcite. No aragonite was noted, and chemical analyses show only a small percentage of magnesium oxide. Siliceous fragments and pebbles in the caprock are residual from parent-limestone gravels and consist of quartz, quartzite, chert, and jasper in about that order of abundance.

A complex history of brecciation, solution, precipitation, and cementation is recorded by almost all caprock sections. The polished surface shown in figure 4 is typical and indicates the following sequence of events: (1) brecciation of crystalline travertine *A* and solution of the margins of fragments; (2) deposition of sandy banded travertine *B;* (3) brecciation (?) and solution; (4) deposition of sandy caliche *C;* (5) brecciation and solution; (6) cementation by sandy matrix *D;* (7) formation of travertine veinlet *E;* (8) brecciation and solution; (9) deposition of manganese oxide glaze; (10) deposition of brown banded travertine *F* and associated manganese oxide streaks; (11) solution; (12) deposition of sandy matrix *G;* (13) brecciation and solution; and (14) cementation by sandy matrix *H*. A similar sequence, though less complicated, is shown by the thin section in figure 5. The thin section also emphasizes textural contrasts primarily due to differences in impurities and crystallinity and the fracture outlines of calcite veinlets and vugs.

FIG. 6.—Nodule from chalky caliche zone with cupped limestone pebble (*solid*) enclosed in travertine crust. The travertine layers represent differences in purity and crystallinity. The inner band is darker reddish-brown, dense travertine; the outer crust is a porous, chalky caliche. Width of specimen is 1.5 inches. Caliche pit, 2 miles southwest of Acme, N.M., along U.S. Highway 70.

Chalky caliche.—Textures and structures in the chalky caliche below the caprock are not so well defined as are those above. The nodules in the upper part of the zone have cores of banded or dense

sandy caliche similar to that of the caprock and are enclosed by concentric laminae of travertine. Commonly the outer crust is tuffaceous and chalky, and the innermost band is a dense brown travertine. In most specimens there are inclusions of older caliche and solutional surfaces between travertine crusts. In the lower part of the zone the nodules give way to solution-cupped limestone pebbles and nodules encased in travertine crusts which are thickened at the bottom (fig. 6). The cupped nodules, which lie near the top of the cupped zone, indicate an overlap in processes of cupping and nodule development. A porous, punky, impure caliche forms the matrix and extends downward into the parent-limestone gravel.

TABLE 1

WEIGHT PERCENTAGES OF ACID-INSOLUBLE RESIDUE IN CALICHE OF NEW MEXICO

Caliche caprock:	
Llano Estacado	
1. Lovington	Trace
2. Maljamar	1.8
3. Kermit	2.9
4. Santa Rosa	3.1
5. Yeso	2.1
Sacramento plain	
6. Vaughn	2.1
7. Mesa	2.4
Diamond A plain (?)	
8. Chaves	Trace
Mescalero plain	
9. East of Roswell	3.0
10. Rock House	3.8
Blackdom plain	
11. Hope	Trace
Younger surface	
12. Carlsbad	8.7
Average	3.33
Nodular caliche:	
13. Llano at Caprock	39.8

INSOLUBLE RESIDUES

The weight percentages of residues insoluble in dilute acid in the caprock range from a trace to 8.7, and in nine measurable samples the average was 3.33 (table 1). In one sample from the nodular zone the percentage was 39.8. Most of the residue is fine sand and silt, with an average estimated percentage of 85.4 quartz particles. Polished and pitted grains were noted in four samples, and rounded grains were prominent in eight samples out of the thirteen. Minor percentages of the residue consist largely of chert, chalcedony, dark minerals, iron oxides, and clay-size particles. There is no indication of volcanic ash, such as was reported from residues of caliche near Lubbock, Texas (Sidwell, 1943). More than half the quartz grains are angular, and many are subhedral, indicating a derivation from weathering of crystalline rocks. The possible importance of mechanical weathering during calichification is suggested by the dominance of silt and fine sand-size particles.

ALTERATION OF CALICHE

At most localities in southeastern New Mexico there is evidence that the caliche formed under earlier climatic regimes and has undergone extensive alterations in Recent time. This evidence consists of solution features, degraded caliche profiles, relations to present soils, and surface alterations of the caprock. Other alterations include structures due to expansion and development of concretionary masses.

SOLUTION FEATURES

Irregular solution cavities penetrating downward into the caliche are common features where there are overlying noncalcareous soils or unconsolidated deposits (pl. 4, *B;* figs. 7 and 8). The cavities vary in length from a few inches to several feet and are filled with the overlying deposits mixed with caliche frag-

ments. In many places the cavities are lined with a thin crust of crystalline travertine. The shapes of some of the cavities (pl. 4, *B*) suggest that they may have been determined originally by roots and in some cases by animal burrows. Relict solution cavities and fills were noted at several localities and indicate the cavities and of zones of caliche fragments within the fill. Unaltered, dense, brecciated caprock forms bosses on the floor of the pit. The shapes and dense composition of nodules and fragments in the fill and in the degraded caliche indicate differential solution of original caprock structures.

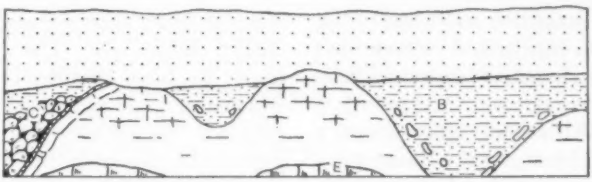


FIG. 7.—Solution cavities in caliche pit, ½ mile south of Kermit, N.M. *A*, reddish-brown, sandy and silty alluvium; *B*, red silt with caliche fragments; *C*, caliche fragments and nodules in travertine-lined cavity; *D*, chalky caliche with rude layers; *E*, dense travertine caprock. The exposure is about 10 feet high.

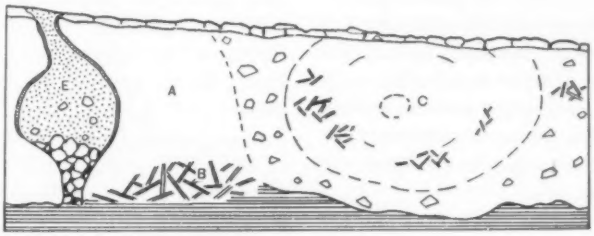


FIG. 8.—Solution cavity and concretionary structure in road cut, 1 mile south of Tower Hill, N.M. *A*, buff, chalky caliche; *B*, breccia of fragments of underlying Permian red beds cemented with caliche; *C*, dense, concretionary caliche with relict breccia of red bed fragments; *D*, brecciated caliche; *E*, solution cavity with travertine lining, filled with soil and caliche fragments. The exposure is 8 feet high.

that at least some solution preceded the latest stages of calichification.

Features due to solution, slumping, and filling are well shown in a caliche pit on the Llano near Kermit, where decomposed caliche is overlain by dune sand and slope-wash deposits (fig. 7). Broad, funnel-shaped cavities lined with travertine descend below the level of the pit floor and are filled with residual red silt and caliche fragments and nodules. Slumping due to solution is evidenced by steep dips of the caliche at the margin of

Solution features on a larger scale, represented by basins and broad shallow valleys, are well known on the Llano caprock (Price, 1940*b*) but are less conspicuous on younger surfaces.

The caliche associated with the solution features is commonly soft and porous, as compared with sections in which overlying soils and surficial deposits are absent. Its derivation from normal caliche is indicated by its gradation downward into unaltered caliche and by relict structures of the caprock and nodular

zones. In some caliche sections, where solution is not clearly evidenced, it is possible that the porous caliche represents a normal transition into the *B* zone of the caliche profile.

RELATION TO PRESENT SOILS

Numerous exposures in the area, especially on the Llano and the Mescalero plains, show gradation of present soils downward into caliche and indicate that the caliche is the parent-material from which they were derived. A typical section on the Mescalero plain shows a downward gradation of (1) a thin organic zone, (2) silty sand with calcareous veins and nodules, (3) chalky nodular caliche, and (4) dense caprock. This condition appears to exist over wide areas of the southern High Plains, and pedologists regard caliche as parent-material for many soils in the region (Marbut, 1923, p. 66; Hawker, 1927; Harper and Smith, 1932, pp. 18–19). Many other soils have been developed from younger sediments deposited on the caprock (Harper and Smith, 1932, p. 16).

SURFACE ALTERATIONS

Where the caprock is exposed at the surface, as is the case over wide areas, it is broken into angular blocks and constitutes a surface rubble. The upper surfaces of these blocks are cupped and faceted by solution, and their sides and bottoms are encrusted with later additions of a pustulose, spongy caliche (pl. 4, *A*). These features are clearly the results of well-known processes of solution-faceting (Bryan, 1929) under present climatic conditions. Continued for an adequate time under sufficiently vigorous climatic conditions, such fragmentation and solutional wastage on the surface with accompanying deposition of subsurface crusts in cracks should produce the banded and brecciated texture exhibited by caprock caliche.

EXPANSION STRUCTURES AND CONCRETIONARY MASSES

Deformed layers and breccias due to expansion of the caliche or underlying shales are known at several localities. In places this is accompanied by development of dense caliche masses within the chalky caliche zone. The expansion appears to have resulted largely from weathering and impregnation of calcium carbonate during later stages of calichification. It is probable that a considerable proportion of the breccia of the caprock is due to earlier action of this process as well as to desiccation.

Lenticular masses of dense, banded, and brecciated caliche up to 10 feet in length occur in the Ogallala caliche and represent the "algae reefs" described by Price, Elias, and Frye (1946). Several masses well down in the chalky caliche zone are exposed along N.M. Highway 83 at the Llano scarp, 1 mile east of Maljamar (pl. 1, *B*, *C*). Rude layers in the enclosing caliche curve irregularly around the lenticular masses. But this enclosing laminated caliche may also pass through the enclosed central mass in a way that demonstrates consanguinity with the laminae wrapping around tops and sides of caliche slabs along N.M. Highway 83, east of Maljamar. Such crossings of the larger mass are crack-fillings, not organic precipitates; and unbroken continuity of their laminae with those enclosing the central mass is demonstrable. The structure of the central mass is that of a dense, laminated, travertine breccia similar to the caprock. Similar masses occur in a caliche pit along the same highway, about 11 miles to the east, and along N.M. Highway 31 at the Llano scarp, 12 miles northwest of Maljamar. Ovate

masses of dense caliche containing large angular fragments were also noted farther north in a caliche pit, 1½ miles west of Kenna (fig. 1). At this locality deformation of the enclosing softer caliche by expansion is evidenced by low domes on the floor of the pit. The upper surfaces of the domes are marked by septarian-like fractures filled with banded travertine.

A spherical mass of less dense caliche with concentric fractures was noted in younger degraded chalky caliche on the Mescalero plain, 1 mile south of Tower Hill (figs. 1 and 8). This structure is clearly concretionary and is surrounded by a zone of breccia, evidencing expansion during its growth. It suggests an early stage of concretionary growth which might later give rise to the reef-like masses described above.

ORIGIN OF CALICHE

GENERAL SUMMARY

Calcareous caliches appear to be a world-wide feature of arid and semiarid regions, and a formidable literature by pedologists, geologists, and geographers could be assembled. Caliche or calcareous surface crusts and hardpans are reported from the Great Plains south of Nebraska and throughout the Southwest (Blake, 1902; Lee, 1905, p. 107–111; Marbut, 1923, p. 66; Udden, 1923; Gould and Lonsdale, 1926, pp. 29–33; Trowbridge, 1926; Hawker, 1927; Breazeale and Smith, 1930; Elias, pp. 136–141, Price, 1933; Sayre, 1937, pp. 65–72; Schoff, 1939, pp. 79–83; 1943, pp. 100–113; Smith, 1940, pp. 44–45; Frye, 1945, pp. 89–91; Price, Elias, and Frye, 1946); Mexico (Price, 1925); Argentina (Kashirsky, 1938); South Africa (Du Toit, 1939, pp. 407–408); Libya, Tunis, Morocco, Algeria, Syria, Egypt, Palestine (Glinka, 1927, pp. 157–159); Arabia (Miller, 1937); and Australia (Woolnough, 1928*a;* 1928*b;* 1930).

Numerous theories have been proposed for the origin of caliche-like materials, and it is unlikely that any one theory is of general application. Most of the theories proposed are included in one or more of the following groups:

1. Deposition in extensive shallow lakes by algae and inorganic processes, as proposed for the Ogallala caprock by Elias (1931, p. 141; 1948, p. 611)
2. Deposition in small disconnected lakes and ponds by physical and/or organic processes (Theis, 1936; Frye, 1945, pp. 91–95)
3. Deposition along streams, especially intermittent streams, by physical and/or organic processes (Trowbridge, 1926; Price, Elias, and Frye, 1946)
4. Deposition by rising artesian waters either at the water table or at the surface (Blake, 1902)
5. Deposition by capillary rise of water from the water table, especially under conditions of high water table (Lee, 1905, pp. 107–111) or a rising water table brought about by aggradation (Theis, 1945)
6. Deposition in the *B* zone of the soil profile by descending surface waters or by capillary rise of surface waters following saturation of the soil zone (R. H. Forbes, quoted in Lee, 1905, p. 110; Glinka, 1914, pp. 157–159; Marbut, 1923, p. 66; Udden, 1923; Gould and Lonsdale, 1926, pp. 29–33; Hawker, 1927; Price, 1933, 1940; Sayre, 1937, pp. 69–70)
7. Various combinations of the above (Lee, 1905, pp. 107–111; Trowbridge, 1926; Breazeale and Smith, 1930; Price, Elias, and Frye, 1946)

All these theories have been applied to caliche in the High Plains and the South-

west, and all except the artesian theory have had recent proponents.

ORIGIN OF CALICHE IN SOUTHEASTERN NEW MEXICO

General statement.—Any satisfactory explanation of the caliche in southeastern New Mexico must account for the following features: (1) the profile development recorded by caliche zones; (2) variations in the profile determined by parent-material and physiographic position; (3) presence of siliceous residual pebbles throughout the profile; (4) caliche of various ages on four different physiographic surfaces and on intervening slopes; and (5) fundamental similarities in the profiles and textures in caliches of various ages; (6) continuity and wide lateral extent, especially on the Llano surface; and (7) occurrence of concretionary and banded "algae-like" structures.

Lacustrine hypotheses.—The lacustrine hypothesis for the Ogallala caprock, as first presented by Elias (1931, pp. 136–141), proposed that the caprock differed from true caliche and was deposited largely by algae in extensive shallow lakes on the surface of the High Plains. Algae cells belonging to the genus *Chlorellopsis* were identified from banded structures in the caprock. Later the caprock was traced southward as an essentially continuous "key bed" into the Llano of southeastern New Mexico, and algal reefs as well as smaller algal structures were described (Price, Elias, and Frye, 1946). Modifications of the hypothesis, restricting the lakes to small, discontinuous bodies of water, were proposed by Theis (1936) and Frye (1945, pp. 91–95).

The difficulty of explaining extensive ponding on the sloping constructional surface of the High Plains has been pointed out by Smith (1940, pp. 90–91) and in itself could be considered fatal to the hypothesis of extensive lakes. There remains, however, the question of whether algal structures are present and, if so, of their distribution and relative importance. Because most of the features noted above either are definitely not of algal origin or are more readily explained by other processes, it is believed that, if algae were present at all, they were of very minor importance. Structures similar to the described "algal" structures have been found in the caliche of several successive physiographic surfaces. They are not a stratigraphic marker in southeastern New Mexico. There is no reason for considering the Llano caprock as distinct from caliche caprocks on younger surfaces. It differs only in exhibiting a more advanced stage of development.

Fluvial hypothesis.—Deposition of calcareous crusts along streams is known to occur in southern Texas and New Mexico and has been considered in combination with other processes (Trowbridge, 1926; Price, Elias, and Frye, 1946, p. 1746). Recent rimstone tufa and calcareous crusts on stream cobbles were observed by the writers in the Pecos River near Loving, New Mexico, and in Black River near Black River village, New Mexico (fig. 1). Encrustations of this type, however, have none of the features of the caliche profile and are distinct from the deposits described above.

Ascending ground-water hypotheses.—Deposition by capillary rise of water from the water table cannot be dismissed because of present low water tables in the area. These levels were much higher before dissection of the surfaces occurred and also during the pluvial stages of the Pleistocene. The facts which debar accepting this explanation include (1) solution-cupping of the upper surfaces of limestone pebbles; (2) occurrence of siliceous residuals; (3) downward penetra-

tion of caliche into impervious shales; and (4) occurrence of caliche on slopes where solutions could never be brought to the surface by capillarity. Under favorable physiographic conditions, capillary water may have augmented deposition from descending soil water in the lower part of the profile, but it could hardly explain the important lowering of the surface by weathering and solution which is indicated by the siliceous residuals.

Pedologic hypothesis.—Most of the features described in the present paper clearly indicate that soil-forming processes were of major importance in producing the caliche in southeastern New Mexico. The first five features noted at the beginning of this section strongly support this explanation. In particular, the caliche profile is a significant soil feature and very difficult to explain by any other hypothesis.

The profile development is believed to be best explained by conditions of alternating saturation and desiccation in a relatively dry climate with periodic rains. Solution occurred as the soil waters moved downward during a rainy period, and precipitation took place with the capillary rise of saturated alkaline solutions as the soil zone dried out. The solution-cupping on the upper surfaces of pebbles in the profile and caliche crusts on their undersurfaces clearly record these processes. The depth of the profile was probably determined by the maximum penetration of soil water and by the cumulative effect of periods of alternating saturation and desiccation of varying intensities. Variation in the depth and maturity of the profile on surfaces of different ages constitute a graded series and (fig. 3) appear to be due to these differences in age rather than to successively shorter independent periods of calichification. From this it follows that caliche formation continued after dissection of the higher surfaces and consequent regional lowering of the water table had occurred and therefore cannot be related to capillary rise of moisture from the water table. Overlapping of zones of solution and deposition is indicated by solution-cupped nodules in the upper part of the chalky caliche zone. A general lowering of the ground surface during caliche formation, as emphasized by Price (1933, p. 505), is evidenced by the siliceous residuals in the caliche, especially where the parent-limestone gravels have been completely removed by the process.

The banding, the brecciation, and the manganese oxide rims in the caprock are believed to record repeated cycles of desiccation and rainfall, with many light rains which penetrated only the caprock zone of the profile. Under these conditions brecciation could have resulted both from drying-out of the soil zone and from expansion accompanying impregnation of caliche. The manganese oxide rims could have formed as a desert varnish. It is probable that these processes went on under a thin soil cover, although at present the *A* zone has been stripped away and the *B* zone, as caliche, is exposed at the surface over wide areas.

AGE AND CLIMATIC IMPLICATIONS

Differences in the age of the caliche are evidenced by stratigraphic relations, physiographic position, and variations in the caliche profile. The Ogallala caprock in western Texas, which is continuous with that in the area studied in New Mexico, is older than the Blanco beds and is thus post–middle Pliocene to pre–early Pleistocene in age (Evans, 1948). Caliche on the Sacramento plain occupies a probably equivalent physiographic position and would be of comparable age. Younger caliches on the lower Mesca-

lero–Diamond A, the Blackdom, and the Orchard Park plains cannot be dated so accurately but doubtless were initiated during interglacials of the Pleistocene. It is probable that profile formation, interrupted by climatic changes, has continued on all surfaces into Recent time.

The climatic implications of caliche as a polygenetic fossil soil have been pointed out by Bryan (1943), who considers successive caliches the record of relatively arid conditions, and solution features as the record of relatively humid conditions. This interpretation is supported by the occurrence of caliche in arid and semiarid regions throughout the world and seems much more probable than Theis's (1936) suggestion that the Ogallala caprock was deposited under Pleistocene pluvial conditions.

On the basis of the above, the caliche sections in southeastern New Mexico indicate the sequence of events shown in table 2. This sequence is obviously tentative, and a definite correlation with the important climatic changes of the Pleistocene is unwarranted, largely because of uncertainties in dating erosion surfaces. The sequence is significant, however, in indicating that further investigations of complex caliche profiles, together with geomorphic studies, may reveal a relatively complete record of climatic changes in the region. The record provided by most caliche sections is likely to be incomplete, and it remains to discover critical sections and to correlate events over wider areas before a satisfactory chronology can be proposed.

TABLE 2

TENTATIVE SEQUENCE OF PEDOLOGIC AND GEOLOGIC EVENTS

Time	Climate	Pedologic Events	Geologic Events
Recent	Relatively arid	Deposition of small caliche nodules in B zone of present soils	
	Relatively humid	Development of solution channels and degraded caliche	
	Relatively arid	Calichification of older solution-channel fills	
	Relatively humid	Development of older solution features	
Pleistocene	Alternating relatively humid and arid	Development of caliche on younger surfaces and continued development of Ogallala caprock	Erosion of Orchard Park, Blackdom, and Mescalero–Diamond A plains; deposition of Gatuna formation and Blanco beds
Late Pliocene	Relatively arid	Initial development of Ogallala caprock	
Middle and early Pliocene	Relatively humid		Deposition of Ogallala formation

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TOPOGRAPHY AND SEDIMENTS OF THE ARCTIC BASIN[1]

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ABSTRACT

Contours of the Arctic Basin were based on a compilation of all known soundings, largely from recent Russian expeditions. Additional general inferences regarding the bottom topography were derived from indirect considerations, such as distribution of Pleistocene glaciers, character of land topography, positions of earthquake epicenters, and sources and composition of the bottom sediments. It is concluded that the floor of the basin is far more irregular than is indicated by the present sparse soundings. Off Alaska and Canada the basin is deepest and least well sounded.

INTRODUCTION

The current international interest in the Arctic demands a more complete knowledge of that area than is generally available at present. One of the least-known aspects is the submarine topography of the Arctic Basin. To some extent it is possible to supplement the sparse soundings by indirect lines of evidence. The writer has attempted to summarize the existing information mainly in an effort to stimulate the collection of additional data. In this he has been aided by conversations with Dr. R. H. Fleming, of the United States Navy Hydrographic Office, and with Dr. R. S. Dietz, of the United States Navy Electronics Laboratory. Much general information about the Arctic is presented in a symposium on polar research edited by Joerg (1928), in a summary of Russian activity by Taracouzio (1938), and in a United States Navy orientation pamphlet by Shelesnyak (1947).

SOUNDINGS

The most direct method of determining the character of the sea-floor topography is through the study of soundings; but, in the Arctic, sounding operations have been hampered by sea ice. The edge of the permanent ice pack, as shown by the *Ice Atlas of the Northern Hemisphere*, coincides fairly well with the outer edge of the continental shelf. Few ships are strong enough to penetrate this ice, so soundings in the main basin are sparse. The continental shelf, however, is mostly covered only by seasonal ice; therefore, it is relatively open to shipping during the summer and is fairly well sounded. Because of their relative abundance, soundings shallower than 500 fathoms are not indicated on the accompanying chart, although the 100-fathom contour based on them is shown.

Ships which reach the edge of the permanent ice pack usually find depths suggestive of the beginning of the continental slope. In 1913 the "Karluk" took nine deep soundings in open water north of Alaska before becoming imprisoned in the ice and eventually being crushed off Siberia (Stefansson, 1921). While the "Karluk" was in the ice, several deep-sounding casts were made, but all failed to reach bottom. Similarly, a large number of additional soundings have been taken in open marginal waters near Spitsbergen, mostly by Danish ships.

The thickness of the permanent ice pack ranges up to about 15 feet, making it practically impenetrable to shipping.

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Consequently, soundings in the central area of deep water have had to be obtained by unusual methods of traveling on, above, below, or with the ice rather than through it. The earliest method of traveling in the Arctic was by sledge and dog team, and some soundings have been obtained on such trips. During his dash for the North Pole in 1909, Peary took several soundings north of Grant Land. He attempted a sounding within a few miles of the pole, but the line broke when 1,500 fathoms had been paid out. Stefansson (1921) in his various trips over the ice also made a number of soundings. Most of them, however, were in depths shallower than 500 fathoms and thus are not indicated on figure 1. His work was largely confined to the Beaufort Sea and the area west of Grant Land.

Another method of traversing the Arctic is that of freezing a ship into the ice so that it drifts with the ice pack. A number of ships not specifically built for such purposes have been accidentally imprisoned and finally crushed; but the drift of their wreckage and other considerations showed that the ice itself is moving toward the Greenland Sea, where it melts. To make use of this drift, the "Fram" under Nansen's leadership was intentionally frozen into the ice pack north of the New Siberian Islands in 1893. During its three-year drift toward the Greenland Sea, eight wire-sounding casts reached bottom. Similarly, the Soviet icebreaker, "G. Sedov," under R. L. Samoilovich, drifted from 1937 to 1939, while the "Sadko," under Ioffe, was in the ice during two periods, 1935 and 1937–1938. About 55 wire soundings accompanied dredgings and other oceanographic observations (Buynitsky, 1940; Zubov, 1940; Gorbunov, 1946). Three main areas were investigated: north of the New Siberian Islands, north of Fridtjof Nansen Land, and off the Taimir Peninsula.

A third method of sounding in the area of ice pack was initiated in 1927, when Wilkins landed an airplane on the ice about 550 miles northwest of Point Barrow. He obtained a single echo sounding of 2,975 fathoms, the deepest reported in the Arctic Basin. In 1941 four more echo soundings north of Wrangell Island were made, along with other observations, by Akkuratov, who landed on the ice at three different localities (Sverdrup, Johnson, and Fleming, 1942; Akkuratov, 1948).

A fourth, intermediate, method was followed in 1937 and 1938, when four Russian scientists under Papanin's leadership were landed near the North Pole and were supplied by airplanes as they drifted on the ice toward the Greenland Sea. Many observations, including 16 deep soundings, were made (Shirshov, 1938, 1940; Papanin, 1939). Papanin's book is of considerable interest because it shows how thoroughly even excellent scientific work in Russia may be pervaded by communistic ideology.

Still another method of sounding was proposed for the "Nautilus" expedition of 1931, whereby a submarine would travel beneath the ice, coming to the surface in the open leads of the ice pack.

Soundings obtained by these various methods comprise a total of 152 deeper than 500 fathoms. This number amounts to only one per 12,000 square statute miles of area; but, unfortunately, instead of being well distributed, most of the soundings are concentrated in a few small areas. The positions of all soundings deeper than 500 fathoms are indicated by small circles on figure 1. Because of the difficulties of navigation in the Arctic, some of these positions are likely to be of rather low accuracy. The wire-sounding

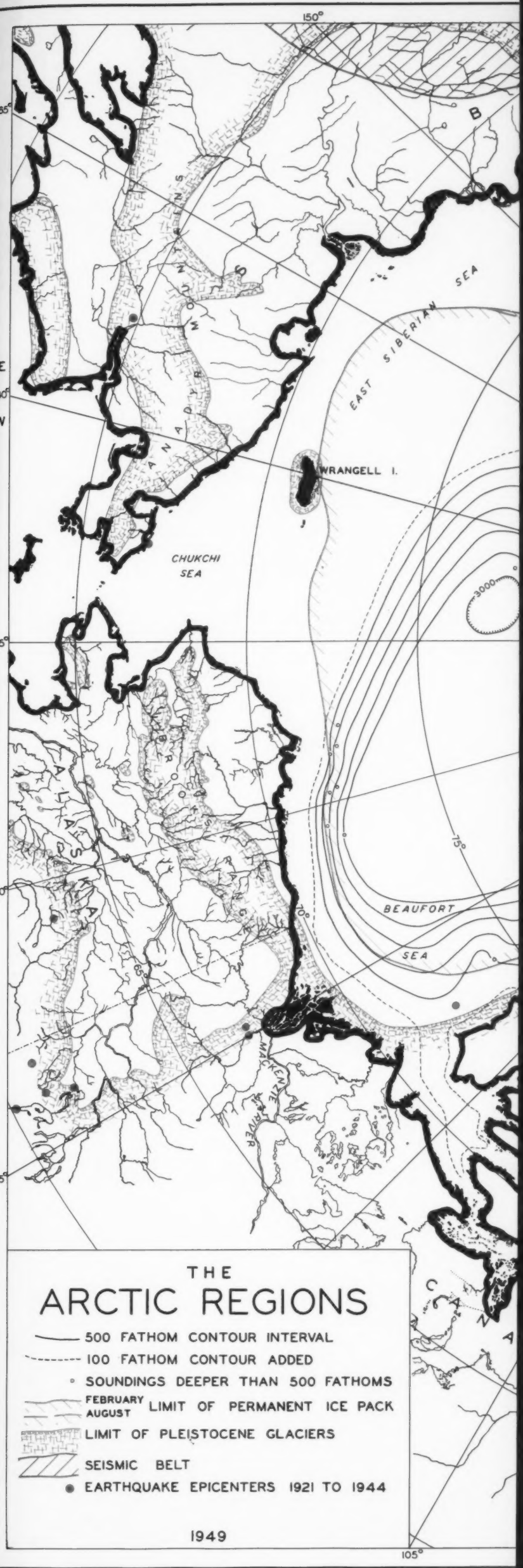
casts which failed to reach bottom are not shown, although they are of some value as indicators of minimum depth.

Depth contours at 500-fathom intervals were drawn for the Arctic Basin and for comparison in part of the north Atlantic Ocean as well. The 100-fathom contour where known is given as a dashed line. Off northeast Greenland it was taken from a new chart by Kiilerich (1945), who apparently based his contours on some unpublished Danish soundings. It is notable that the general form of the basin, as indicated by present data, is little different from that inferred by Nansen (1904) on the basis of only a few soundings. Where soundings are sparse, the present contours are smoothly curving, but in densely sounded areas they are more irregular and probably more nearly depict the true bottom configuration. The soundings taken by Akkuratov about 500 miles north of Wrangell Island are of especial interest, because they indicate the presence of a deep ridge which may extend completely across the Arctic Basin. The deepest part of the basin is near Bering Strait, in the least well-sounded region. Two recent contour maps show irregular and complicated topography in this area because the cartographers failed to recognize that the small bar and dot printed above some of the soundings on various charts indicate that no bottom was reached within the length of the available sounding wire. A 3,000-fathom contour was drawn in the bottom of the basin on the basis of the near-by deepest sounding of 2,975 fathoms.

GLACIAL EROSION

During the Pleistocene epoch glaciers from Greenland, Canada, and parts of Siberia radiated outward from their growth centers. Movement north of the centers was toward the Arctic Ocean, as shown by radiating glacial striae and other markings. According to Flint (1945, 1947, pl. 3), they reached beyond the present coasts from the Taimir Peninsula westward past Norway and Greenland to eastern Alaska. A minor exception is the northernmost tip of Greenland, which is unglaciated. Along most of this distance typical fiord shorelines are common. Off-shore islands in this area, such as North Land, Nova Zemlya, Fridtjof Nansen Land, and Spitsbergen were also glaciated. It is noteworthy that the sea floor between the islands and the mainland is very irregular and contains numerous troughs, which Nansen (1904) long ago recognized as being of probably glacial origin. The heads of some troughs extend close to the fiord coasts of the land and thus may be extensions of the fiords. Scattered about between the troughs are many banks and small islands, which may well be erosional remnants of glaciation. Though the area is not densely sounded, it is evident from the available data that this part of the shelf is much more irregular than are normal continental shelves. The largest areas of irregular shelf are in the Barents and the Kara seas, which are unusually deep shelves, generally exceeding 150 fathoms. Because of these relationships, figure 1 indicates that the areas covered by the ice sheet should possibly be extended beyond the limits shown by Flint's maps to include both the Barents Sea and the Kara Sea. The erosion could have taken place in water shallower than at present if it had occurred before isostatic depression of the shelf beneath the ice load. The glaciers in part may have moved northward from the mainland, as is suggested by the long trough east of Nova Zemlya. The fiord coasts of the islands indicate supplementary glacial erosion from these centers.

165°
E
180°
W
165°
150°
135°



THE ARCTIC REGIONS

- 500 FATHOM CONTOUR INTERVAL
- 100 FATHOM CONTOUR ADDED
- SOUNDINGS DEEPER THAN 500 FATHOMS
- FEBRUARY / AUGUST LIMIT OF PERMANENT ICE PACK
- LIMIT OF PLEISTOCENE GLACIERS
- SEISMIC BELT
- EARTHQUAKE EPICENTERS 1921 TO 1944

1949

135°
120°
105°
LENA RIVER
LAPTEV SEA
NEW SIBERIAN ISLANDS
SEA
500
1000
1500
2000
2500
3000
85°
80°
75°
2500
2000
1500
1000
500
CANADA
90°
75°

FIG.

105°
90°
75°
PENINSULA
KARA SEA
NORTH LAND
NOVAYA ZEMLYA
FRIDTJOF NANSEN LAND
BARENTS SEA
SPITSBERGEN
GREENLAND SEA
2000
1500
1000
500
GREENLAND
BAFFIN BAY
500
1000
1500
75°
60°
45°

FIG. 1

60°

RUSSIA

BARENTS SEA

FINLAND

SWEDEN

NORWEGIAN SEA

ICELAND

2000

1500

1000

500

45°

45°
30°
15°
0°
15°
30°
N
E
W
1000
1500

The shelf off Greenland and Canada is much less well sounded, but it is apparent that at least some of the deep troughs which separate the land into large islands extend seaward across the narrow shelf. Spencer in 1905 ascribed some of these submarine troughs in part to glacial erosion. Since that time almost no additional soundings have been obtained to show whether other troughs are present.

From eastern Alaska westward past Bering Strait to Taimir Peninsula the continental shelf is shallower, mostly less than 80 fathoms, and extremely flat. This flatness was noted by Nansen, who remarked that ships sailing off Siberia were subject to little danger of running aground, even though the water is not deep. Recent investigations with recording echo-sounders in the Bering Sea and the Chukchi Sea indicate that these areas are among the flattest in the world (LaFond, Dietz, and Prichard, 1949). This flatness, together with the fact that the northern border of the Pleistocene ice sheet in both Siberia and Alaska is well inland, suggests that the continental shelf there was never subjected to much glacial erosion, although Flint indicates that Wrangell Island and the New Siberian Islands were covered by glaciers.

TOPOGRAPHY OF ADJOINING LAND

Some information regarding sea-floor topography may be provided by the seaward projection of land mountain ranges. A general topographic map of the North Polar region by Joerg (1930) shows that the Brooks Range of Alaska and the Anadyr Mountains of Siberia are essentially parallel to the coast and do not extend seaward. This is the usual relationship for Suess's Pacific type of coasts. The Khayakhak and Kharaulakh Mountains of Siberia and the Ural Mountains, which continue through Nova Zemlya, however, are almost at right angles to the coast (Atlantic type) and may therefore be reflected in local outward projections of the Arctic Basin margins, like the one north of the New Siberian Islands. The various ranges are separated by geologically quiescent shield areas, from which one would expect few structural projections into the basin. These shield areas are also characterized by broad, nearly flat plains bordering the ocean. An excellent discussion of the general geology of the Arctic region was presented by Eardley (1948), who drew on structure, stratigraphy, and paleontology to outline the paleogeography of the area. He concluded that the basin is underlain by continental rocks which began to sink in late Paleozoic time. Gutenberg and Richter (1939) state, however, that the amplitudes of reflected longitudinal earthquake waves probably indicate the presence of bottom material like that of the Pacific Ocean and unlike that of the continents. Unfortunately, the seismic velocity measurements needed to verify the character of the basement are lacking at present (Gutenberg and Richter, personal communication).

EARTHQUAKE EPICENTERS

It is well known that most earthquake epicenters fall along fairly well-defined belts, which also are areas of volcanic activity and mountain-building and thus are characterized by irregular rugged topography. The Mid-Atlantic Ridge is such an area. Various Russian workers and others have shown that the belt of epicenters related to the Mid-Atlantic Ridge continues northward from south of Iceland past Spitsbergen and along the European side of the Arctic Basin to the Lena River region, where it may meet the Kharaulakh and the Khayakhak mountain ranges. Figure 1 shows the epi-

center belt taken from a map reproduced by Heck (1938) from Russian sources. This is based on seismic data prior to about 1925. Gutenberg and Richter (1941, pp. 70–73; 1945) indicate that some of these epicenters may be poorly located, but the epicenters which they do consider acceptable follow the same general trend, except for a few scattered ones, chiefly near Bering Strait. The latter belong to the circum-Pacific belt of activity. Their epicenters, shown by large dots on figure 1, are of earthquakes which occurred between 1921 and 1944. Because most of them postdate the belt shown by Heck, they serve as an excellent check. All but two of the reported shocks are of less than magnitude 7, and consequently they are not considered major earthquakes. The fact that the belt extends from an irregular submarine mountain range across the poorly known Arctic Basin suggests that the topography of the part of the basin through which the belt passes may also be irregular.

SEDIMENTS

It appears that sediment descriptions for only six samples from deeper than 500 fathoms in the Arctic Basin are available; although it is possible that data for others have been published in Russian reports inaccessible at present. Five of the samples were collected aboard the "Fram" in 1893–1895 from northwest of the New Siberian Islands. Four of these are from depths between 1,950 and 2,200 fathoms. The sediments are very fine-grained, containing less than 0.1 per cent of grains coarser than 1 mm. and more than 60 per cent of grains finer than 0.01 mm. (Bøggild, 1906). All were named "gray clay," although a strong brown tinge was present. Only one sample contained appreciable organic material, but even this one had less than 4.5 per cent of *Globigerina* tests. The description of grain size, grain composition, and chemical analysis is such that all five samples could easily be "red clay," like the "red clay" of the Pacific Ocean, which also is more brown than red. One of the deep samples which was well described is summarized in table 1, with values recomputed from the original for greater ease of comparison. It should be noted that the chemical composition is just about the same as that given by Sverdrup, Johnson, and Fleming (1942) for 51 samples of "red clay" from the Atlantic, Pacific, and Indian oceans (Steiger's analyses). This particular sample, however, contains nearly equal amounts of ferric and ferrous iron, unlike most of the other Arctic samples, for which ferric is far in excess of ferrous iron—as is characteristic of "red clay." The mineral composition is within the common range of variation of "red clay." Most striking is the absence of volcanic glass shards and of manganese minerals, although the latter may possibly be included with opaque or aggregate minerals. Calcite was present as foraminiferal tests, almost exclusively of *Globigerina*. According to Brontman (1938, p. 277), a sample taken by the Russian North Polar Expedition at lat. 87°10′ N., long. 1° E., 2,381 fathoms, consisted of silt, reddish-brown at the top and gray below. Wüst (1942) also reported that, of 39 deep samples obtained by the "Sedov," at least 26 were brown.

Ten more sediment samples were collected aboard the "Fram" from the continental shelf between the Kara Sea and the New Siberian Islands. All are fine-grained, some as fine as the samples from deep water. Most are also characterized by a brownish color. Nineteen cores obtained by the "Belgica" from the shelf

near Nova Zemlya consist of brown sediment (Thoulet, 1910). Four additional samples from the shelf of the Chukchi Sea were taken by the United States Navy Electronics Laboratory in 1947 (LaFond, Dietz, and Prichard, 1949). Mechanical analyses showed that three of them are very fine-grained, having median diameters between 0.0035 and 0.009 mm.; the fourth sample is much coarser. Limy and siliceous remains of organisms are minor constituents, usually making up less than 1 per cent of the sample. Trask (1932) described 19 more samples from shallow near-shore waters along Alaska and in the Canadian Archipelago and 29 others from deeper water near the south end of Baffin Bay. Nearly all are gray, and many are poorly sorted. Several hundred additional samples from the Barents Sea and the White Sea were briefly described by Gorshkova (1931). Many of these are poorly sorted, and some are brown-colored and contain a high percentage of manganese oxide.

A large amount of additional information on bottom materials of the shelf is available in the form of bottom notations on the excellent large-scale navigational charts recently published by the United States Navy Hydrographic Office (HO 6601-6). These notations are based on the small quantity of sediment which adheres to the tallowed lead weight on sounding lines. Because many different observers collected the data, such notations must be used with caution. Altogether, 158 bottom notations were counted; of these, 115 are listed as "mud" or "clay." Of the 47 notations for which the color is indicated, 32 are brown. Most of these chart notations of color were based on brief sample studies by Bissett (1930), who found that, in the reddish or brownish mud, FeO and Fe_2O_3 constitute 0.13 and 8.14 per cent, respectively, while in

TABLE 1

COMPOSITION OF SEDIMENT FROM LAT. 83°24′ N.; LONG. 102°14′ E.; 1,900 FATHOMS

Mineral Grains Coarser than 0.05 mm.	Per Cent	Chemical Composition		
		Oxide	Arctic Sample (Per Cent)	Average of 51 "Red Clay" Samples (Per Cent)
Calcite	3.83	SiO_2	57.21	54.48
Quartz	2.45	Al_2O_3	15.64	15.94
Augite	0.92	Fe_2O_3	5.05	8.66
Aggregates	0.79	FeO	4.25	0.84
Opaque	0.50	MnO	0.58	
Hornblende	0.32	MnO_2	0.05	1.21
Orthoclase	0.23	CaO	3.56	1. 6
Microcline	0.20	MgO	1.69	3.31
Olivine	0.15	K_2O	2.7	2.85
Plagioclase	0.10	Na_2O	1.96	2.05
Garnet	0.03	P_2O_5	0.26	0.30
Epidote	0.02	H_2O	5.03	7.04
Tourmaline	0.02	Others	2.20	1.36
Zircon	0.02			
Total	9.58	Total	100.22	100.00

the blue or gray mud the values are 3.22 and 0.89 per cent. It is clear, therefore, that the brown color is due to oxidation of the iron. The other bottom notations on the charts are as follows: mud-and-sand, 9; sand, 11; stony, 4; rocky, 8; and various mixtures of mud with stony and rocky, 9. It is notable that the most homogeneous bottom is that of the shelf off Siberia. This area is characterized almost exclusively by mud, except near islands.

There are several agents and corresponding source areas which may contribute sediments to the Arctic Basin. One of these agents is ice. Available evidence indicates that continental glaciers did not reach the present coastline from eastern Alaska westward to the Taimir Peninsula; thus this area of continental shelf and basin could have received no glacial till. In the rest of the circumference of the Arctic Ocean, glaciers did reach the present coast. Judging from the topography of the shelf of the Barents and Kara seas, the glaciers did much active excavation there. Most of the chart notations of mud mixed with stony or rocky material occur in these areas. The poor sorting is suggestive of till, perhaps deposited atop the eroded surface by the retreating glacier. Much more morainic material must have been deposited beyond the zones of excavation, possibly at the edge of the shelf.

Ice-rafting of sediments is widely reported from the Beaufort Sea by Kindle (1924); off Greenland by Tarr (1897) and others; in the East Siberian Sea by Sverdrup (1931); and from the Chukchi Sea by LaFond, Dietz, and Prichard (1949). The sediments are carried primarily by ice floes, which pick them up by bottom-freezing or by ice-shove against the shore. Some sediment transportation is also accomplished by icebergs from glaciers which reach the sea and calve off. River ice is also important. It is noteworthy that these reports of sediment-laden ice are from marginal areas. Nansen (1904) remarked particularly on the absence of coarse sediments on the ice above the deep water of the basin but stated that embedded mud was present. In his opinion, most of this material is transported completely across the basin and deposited east of Greenland, where the ice melts. He considered that only a small amount of it can be released above the basin by bottom-melting or by overturning of the ice.

During the short summer season the melting ice of the land brings the streams to flood, and then they transport much sediment to the coast. The glaciated half of the Arctic coast contains many fiords and deep troughs which serve as settling areas; thus practically no stream-borne sediment should reach the shelf off Europe, Greenland, and northeastern Canada. The rest of the coast, however, is characterized by a number of large streams, such as the Mackenzie and the Lena rivers, which are actively building deltas on the shelf. As these rivers are of low gradient, they carry much fine-grained material, which may reach well beyond the deltas. Possibly this river-supplied fine material is responsible for the wide expanse of mud bottom of the East Siberian Sea. Only a minor contribution is made by wave erosion because waves and even tides are of very small height along most of the shore, owing to friction losses in crossing the wide shelf and to damping action by the ice.

A number of authors have remarked on the strength of the wind radiating outward from the Greenland icecap (Kindle, 1924; Matthes, 1946; Hobbs, 1948), though there is disagreement regarding its origin. Mention is made of the trans-

portation by wind of coarse debris onto the ice to a distance of several miles from land. Thin deposits of dust on the ice many miles from shore have also been noted by Kindle and others, who believed them to consist of volcanic ash or perhaps even of cosmic dust. Prior to present wind transport, widespread deposits of loess were formed during the Pleistocene epoch, when the glaciers were present. Hobbs showed that a wide belt of loess north of the glaciers in Siberia was deposited by northward-blowing winds. The site of similar deposits from Taimir Peninsula westward to eastern Alaska would now be below sea level on the shelf or in the Arctic Basin.

A minor contribution to the sediments of the Arctic is made by inflowing Gulf Stream water carrying various warmer-water organisms. Sponge spicules and other organic debris found in sediments just north of Europe are believed to have this origin (Veen, 1913). The Gulf Stream water continues on into the Arctic Basin, where it forms a layer of relatively warm water sandwiched between top and bottom waters having temperatures below 0° C.

In contrast to the north Atlantic and north Pacific oceans, the deep polar sea appears to be very deficient both in species and in numbers of planktonic algae (Gran, 1900). Nansen considered this lack the result of light reflection and absorption by the thick ice cover. Some discoloration of the ice by diatoms was believed to have resulted from attachment or freezing of the organisms into the ice nearer shore. In the absence of plants, there should be few animals, a conclusion which is confirmed by Bogarov (1946), who reported that study of the "Sedov" material showed that scanty zoöplankton is characteristic of the central part of the Arctic Ocean. This explains the very low percentage of foraminiferal tests in the sediments, although these samples came from depths at which *Globigerina* ooze occurs elsewhere. The discovery of a few polar bears and seals on the ice pack (Stefansson, 1921; Akkuratov, 1948; and others) appears to be contradictory evidence but may mean simply that where the ice cover is locally absent, as in the open leads, life can be abundant. The low percentage of calcium carbonate in the sediments is in agreement with Trask's (1937) statistical studies for other oceans, which indicated that, where surface-water salinities are lower than 34 parts per thousand, the calcium carbonate of the sediments is generally less than 5 per cent. Shirshov (1940) showed that the surface salinities in the Arctic are less than 31.5 parts per thousand.

In summary, a number of agents deposit sediments in the Arctic Ocean. The sea floor between Taimir Peninsula westward to eastern Alaska should be characterized by former direct ice deposits and former wind-laid deposits. The remainder of the coast now receives most of the stream-borne sediments. Ice-rafted sediment and organic debris may be evenly distributed between the two areas. In the writer's opinion, this distribution of effective agents probably is reflected in a somewhat greater rate of deposition in the basin nearest northern Europe than elsewhere. It is noteworthy in this connection that the floor of the basin appears to be somewhat shallower there than off Alaska and eastern Siberia. The fine-grained texture of most of the sediments, both in the basin and on the shelf, together with the prevalent brownish oxidized color, indicates that deposition is very slow, at least at the present time. Probably deposition takes place so slowly that irregularities formed by faulting have not been buried, and therefore the

bottom of the basin, particularly in the belt of epicenters, is far more irregular than is indicated by the generalized contours of figure 1.

CONCLUSIONS

The following tentative conclusions regarding the topography of the Arctic Basin are based on the scanty data outlined above.

1. The shelf and margin of the basin from the Taimir Peninsula westward to eastern Alaska is deep and irregular because of glacial erosion and deposition, while the rest of the shelf is shallow and flat because it was not covered by glaciers.

2. The slope and floor of the basin off Europe may be irregular because of submarine faulting.

3. The basin is oval-shaped, perhaps deepest near Alaska and eastern Siberia, and it may be divided by a structural ridge extending northward from a position between Wrangell Island and the New Siberian Islands.

4. The floor of the basin may be fairly irregular because of the present slow rate of deposition of sediments by all agents.

Unquestionably, much more should be learned of the basin. High on the list stands the need for additional soundings. A line of soundings across the least-known area could be obtained by freezing a ship into the ice near the Beaufort Sea. As pointed out by Zubov (1940) and others, a ship starting there would pass very near the Pole. An excessive amount of time, however, would be required for such a drift. Possibly the soundings can best be obtained by landing small airplanes carrying portable sonic sounders onto the ice at a number of points. This method might be most adaptable to the large unsounded area off Alaska, where airplane facilities have already been established. A method which would yield continuous profiles rather than separate spot soundings would be sounding from a submarine traveling completely submerged beneath the ice, a plan which was contemplated for the "Nautilus" expedition in 1931. Regardless of how they are obtained, future soundings and bottom samples will be valuable to geological knowledge of the Arctic.

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REPLACEMENT AND THE EQUATING OF VOLUME AND WEIGHT[1]

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ABSTRACT

A method is presented for writing molecularly, volumetrically, and electrically balanced equations for replacement reactions. Two general situations obtain: (*A*) enough is known of the chemistry of the particular reaction to write a complete equation, or (*B*) only enough is known to permit the setting-down of the essential facts of the reaction in skeleton form. In the first case a simple, molecularly balanced equation for the reaction in question will show that there are three different possibilities: (1) that too much guest is furnished for the volume left by the departing host; (2) that too little guest is produced to fill the volume of host removed; and (3) that the volumes involved are approximately equal. In the second case the balanced skeleton equation will show that (1) there is a deficiency in the host of the large ions (sulfur, oxygen) needed in an equal volume of the guest; (2) there is an excess of these large ions in the host over the amount that can be used in an equal amount of guest; and (3) the number of large ions in equal volumes of host and guest are the same. In both cases the third category is relatively rare. Methods by which the additional material needed can be provided or the extra material can be removed are suggested. In supergene sulfide replacements the main problems in achieving complete balance are (*a*) a mechanism for the oxidation of excess S^{-2}, (*b*) a source of hydrogen sulfide, and (*c*) a mechanism for the reduction of S^{+6} in solution to provide additional S^{-2}. A naturally present reducing agent which can do the required work is not immediately apparent; the most likely oxidizing agent is Fe^{+3}; H_2S probably derives from the action of H_2SO_4 on certain sulfides. Hypogene sulfide and sulfosalt metasomatic reactions cannot be written in complete form except in a few cases. If such replacements require that sulfur be removed, it is considered to be oxidized to the sulfate ion. If additional sulfur is needed, it is provided directly from the ore-bearing solutions. No attempt is made to show how it got to the scene of deposition. Other replacements than those of sulfides and sulfosalts are produced in equational form, and similar conclusions are reached as to the requirements for putting them in complete balance.

INTRODUCTION

In a recent paper Buerger (1948, p. 114) remarked that "diffusion suggests the mechanism" for volume-for-volume replacement. He goes on to say that replacement is "substantially a matter of diffusion of new metals into the volumes dominated by oxygen or sulfur atoms." This statement is true enough when oxides, silicates, or carbonates are replacing silicates or when sulfides or sulfosalts are replacing sulfides. But it is not applicable to the replacement of silicates, oxides, or carbonates by sulfides. When such replacements occur, sulfur must be substituted for oxygen, and this is a far more drastic process than the exchange of metal ions which are far smaller and whose movements have a smaller effect on the structure of the host mineral. But, because sulfides do replace other classes of minerals, this sulfur-for-oxygen substitution must take place, comparatively difficult though it may be to carry out. Once the guest ion or ions have been brought into contact with the host mineral, it seems reasonable that the actual replacement is accomplished through new material being diffused into, and old material out of, the space originally occupied by the original mineral.

THE PROBLEM OF VOLUME-FOR-VOLUME REPLACEMENT

The acceptance of Buerger's general principle does not solve one problem which has been puzzling geologists ever since it was first realized that replacement was es-

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sentially a volume-for-volume exchange. That problem is to write chemical equations for replacement reactions which, although representing possible and molecularly balanced reactions, also contain equal volumes of solid material on both sides of the equation. The present concept, if the textbooks are consulted, is to say that the equation given indicates what happens in a general way during metasomatism but that, because the phenomenon occurs on a volume-for-volume basis, it does not give an exact representation of the chemistry of the process. A simple example of such an equation would be

$$2Ag^{+1} + SO_4^{-2} + CuS = Ag_2S + Cu^{+2} + SO_4^{-2}. \qquad (1)$$

The actual space occupied by 1 formula unit[2] (molecule) of covellite is 34.24 cubic Ångstrom units (see table 1), whereas that taken up by 1 molecule of argentite is 58.11 Å^3. If the replacement of covellite by argentite occurred exactly as represented by equation (1), there would be a gain of very nearly 70 per cent in volume during the process. Because such a gain of volume does not take place under the conditions of hypogene or supergene metasomatism, it follows that equation (1) must be modified so as to equate not only molecular units but unit volumes as well. In other words, a quantitative approach to the problem should be attempted, in contrast to the qualitative one of equation (1).

SULFIDE AND SULFOSALT REPLACEMENTS—SUPERGENE CONDITIONS

GUEST IN EXCESS

In the preceding paragraph it was shown that the replacement of 1 molecule of covellite (Vol. = 34.24 Å^3) by 1 molecule of argentite (Vol. = 58.11 Å^3) would find 23.87 Å^3 of argentite for which no space would be provided by the removal of 1 formula unit of covellite. These 23.87 Å^3 are 70 per cent of 1 formula unit volume of covellite. This means that 1.7 molecules of covellite must be removed for each molecule of argentite formed by the metasomatic process if no loss of volume is to occur. To eliminate fractions, it would be necessary to multiply the 1.7 molecules of covellite and the 1 molecule of argentite by 10; i.e., 17 molecules of covellite must be taken away for each 10 molecules of argentite deposited. But how are these extra molecules of covellite to be removed? Because the probable solubility of cupric sulfide in the solutions accomplishing this supergene replacement is vanishingly small, it is unlikely that the excess covellite can be removed in simple solution. Some other mechanism, therefore, must be suggested. It would seem that this could easily be the oxidation of the S^{-2} to the S^{+6} of the sulfate radical. As the necessary concomitant of this oxidation, the reduction of ferric ion to ferrous ion should be adequate, as is explained

[2] The unit cell of the average mineral contains more than one molecule. If the volume of the unit cell is divided by the number of molecules (formula units) contained in it, the result will be the volume, in cubic Ångstrom units, of one formula unit of the mineral in question. Fairbairn (1943, pp. 1308–1310) gives a brief and clear explanation of the calculation of unit cell volumes and of the relation of these volumes to density. The formula for the unit cell volume of a rhombohedral mineral is given incorrectly, however, and should be $a^3\sqrt{1 - 3\cos^2 a + 2\cos^3 a}$. In table 1 are given the unit cell volume, the number of formula units in the unit cell, and the volume of the formula unit for each mineral with which this paper deals. The data for calculating these values have been obtained for sulfides, oxides, and native metals from Dana (1944). For calcite, fluorite, alpha quartz, and wollastonite, the necessary data have been taken from Bragg (1937). The results have been compared, when possible, with Fairbairn's (1943, pp. 1317–1319) and are in close agreement.

TABLE 1

Mineral	Unit Cell Volume ($Å^3$)	No. of Formula Units in Cell	Volume per Formula Unit ($Å^3$)
Anglesite ($PbSO_4$)	313.92	4	78.48
Argentite (Ag_2S)	116.21	2	58.11
Bornite ($CuS \cdot 2Cu_2S \cdot FeS$)	1,305.75	8	163.21
Bournonite $\frac{1}{2}(2PbS \cdot Cu_2S \cdot Sb_2S_3)$	543.00	4	135.75
Calcite ($CaCO_3$)	122.06	2	61.03
Chalcopyrite ($CuS \cdot FeS$)	282.81	4	70.70
Chalcocite (Cu_2S)	7,285.79	160	45.54
Copper (Cu)	46.79	4	11.70
Covellite (CuS)	205.46	6	34.24
Enargite $\frac{1}{2}(Cu_2S \cdot 4CuS \cdot As_2S_3)$ or $(3Cu_2S \cdot As_2S_5)$	296.63	2	148.31
Fluorite (CaF_2)	161.82	4	40.46
Galena (PbS)	208.53	4	52.13
Jamesonite ($4PbS \cdot FeS \cdot 3Sb_2S_3$)	1,195.26	2	597.63
Magnetite ($FeO \cdot Fe_2O_3$)	587.22	8	73.40
Polybasite ($4Ag_2S \cdot 4Cu_2S \cdot Sb_2S_3$)	1,164.23	2	582.11
Pyrite ($FeS \cdot S$)	157.90	4	39.48
Quartz (alpha) (SiO_2)	112.28	3	37.43
Silver (Ag)	67.78	4	16.95
Sphalerite (ZnS)	157.46	4	39.37
Stannite ($Cu_2S \cdot FeS \cdot SnS_2$)	319.73	4	79.93
Tennantite ($5Cu_2S \cdot 2CuS \cdot 2As_2S_3$)	1,058.09	2	529.04
Tetrahedrite ($5Cu_2S \cdot 2CuS \cdot 2Sb_2S_3$)	1,102.21	2	551.10
Wollastonite ($CaSiO_3$)	390.00	6	65.00
Zincite (ZnO)	47.13	2	23.56

shortly. To provide the needed ferric ion, it seems reasonable to assume that some ferric sulfate or chloride may have survived the trip down through the zone of oxidation to react with the excess of covellite to form sulfate ion from the sulfide and to be itself changed to ferrous iron. This can be expressed in an equation as follows:[3]

$$\left.\begin{array}{l} 17CuS + 20Ag^{+1} + 10SO_4^{-2} + 56Fe^{+3} + 168Cl^{-1} + 28H_2O \rightarrow \\ (582.08\ \text{Å}^3) \\ \qquad 10Ag_2S + 17Cu^{+2} + 17SO_4^{-2} + 56Fe^{+2} + 112Cl^{-1} + 56H^{+1} + 56Cl^{-1}, \\ \qquad (581.10\ \text{Å}^3) \end{array}\right\} (2a)$$

Volume difference = 0.17 per cent.[4]

The equation just given, (*2a*), can be expressed by far fewer molecules if it is considered acceptable to have a volume difference of between 1 and 2 per cent instead of the quite small amount resulting in equation (*2a*). This is illustrated by equation (*2b*):

$$\left.\begin{array}{l} 5CuS + 6Ag^{+1} + 3SO_4^{-2} + 16Fe^{+3} + 24SO_4^{-2} + 8H_2O \rightarrow \\ (171.20\ \text{Å}^3) \\ \qquad 3Ag_2S + 5Cu^{+2} + 5SO_4^{-2} + 16Fe^{+2} + 16SO_4^{-2} + 16H^{+1} + 8SO_4^{-2}, \\ \qquad (174.33\ \text{Å}^3) \end{array}\right\} (2b)$$

Volume difference = 1.80 per cent.

Here use has been made of ferric sulfate instead of ferric chloride, but the principle remains the same because the oxidizing agent in both instances is ferric iron.

These last two equations—(*2a*) and (*2b*)—depart from the accepted thought on the process of replacement, in that they introduce components on both sides of the equation which, while taking a very definite part in producing a volumetrically balanced product, leave no solid evidence of their presence behind them. This departure from the simple, molecularly balanced equation seems well grounded, in that it permits the equation to equate volumes as well as molecular weights and electrons. The attempt made in these two equations to explain the process by which the excess molecules of covellite, which must be removed to achieve volumetric balance, are got into solution is not backed by experimental proof, but that lack does not invalidate the general method of balancing replacement equations here presented. It is, nevertheless, advisable to consider the possibility of the occurrence of the reaction of equations (*2a*) and (*2b*).

In this paper most of the supergene equations considered are of the type of equation (*2a*). If the equations chosen are representative of supergene reactions, then it is more common for the volume of the replacing mineral or minerals produced (by a

[3] It will be noted that, in this equation and those of the same type which follow, no attempt has been made to achieve balance in terms of the numbers of molecules in the unit cells of the minerals taking part in the reaction. Such unit cell equality can, however, be attained merely by multiplying through the equation by the largest number (of molecules) contained in any one of the unit cells involved. In eq. (*2a*) this number would be six.

[4] It will be found that this equation and those of the same type which follow it are not quite in volumetric balance. The deviations from equality usually are quite small (less than 2 parts in 100), but some have differences up to 3 per cent. Such differences are larger than the limits of error in the determinations of the dimensions of the unit cells used but are allowed to stand because exact volumetric balance would require the use of integers tens or hundreds of times larger than those here accepted.

molecularly balanced equation) to be greater than that provided by the removal of the replaced mineral. To achieve volumetric balance in equations of this kind, solid sulfides, above the amount required for molecular balance of the basic equation, must be dissolved and removed in solution. Primarily, this is a problem of oxidizing some of the sulfide ion of the replaced mineral to the sexivalent sulfur of the sulfate radical. This, it has been assumed, is accomplished by the reduction of Fe^{+3} to Fe^{+2}, the emf of the cell so set up being sufficient to drive the various stages of the reaction forward. It is now advisable to consider in some detail the adequacy of the oxidation potentials of the electronic reactions suggested as taking place when a sulfide ion is converted to sulfate. The half-reactions or electronic reactions used in this section and in the other parts of this paper are given in table 2. From these it can be seen that the oxidation of sulfide ion to sulfate can go forward under the standard conditions

TABLE 2*

Electronic (or Half-) Reaction	Oxidation Potential (Volts)†	Electronic (or Half-) Reaction	Oxidation Potential (Volts)†
$SO_3^{-2}+2OH^{-1}=SO_4^{-2}+H_2O+2e^{-1}$	0.90	$Mo^{+3}(r)=Mo^{+5}+2e^{-1}$	−0.11
$S+6OH^{-1}=SO_3^{-2}+3H_2O+3e^{-1}$	0.61	$H_2S\rightarrow S+2H^{+1}+2e^{-1}$	−0.14
$Cd_2^{+2}=2Cd^{+2}+2e^{-1}$	0.6	$Sn^{+2}\rightarrow Sn^{+4}+2e^{-1}$	−0.15
$Fe(OH)_2+OH^{-1}=Fe(OH)_3+e^{-1}$	0.56	$Cu^{+1}\rightarrow Cu^{+2}+e^{-1}$	−0.17
$S^{-2}=S+2e^{-1}$	0.51	$H_2O+H_2SO_3\rightarrow SO_4^{-2}+4H^{+1}+2e^{-1}$	−0.20
$HS^{-1}+OH^{-1}=S+H_2O+2e^{-1}$	0.48	$Cu\rightarrow Cu^{+2}+2e^{-1}$	−0.345
$Cr^{+2}=Cr^{+3}+e^{-1}$	0.41	$S+3H_2O\rightarrow H_2SO_3+4H^{+1}+4e^{-1}$	−0.45
$Ti^{+2}=Ti^{+3}+e^{-1}$	0.37	$Cu\rightarrow Cu^{+1}+e^{-1}$	−0.52
$Mo^{+3}(g)=Mo^{+5}+2e^{-1}$	0.25	$Fe^{+2}\rightarrow Fe^{+3}+e^{-1}$	−0.77
$V^{+2}=V^{+3}+e^{-1}$	0.20	$Ag\rightarrow Ag^{+1}+e^{-1}$	−0.80
$H_2=2H^{+1}+2e^{-1}$	0.00	$Mn^{+2}\rightarrow Mn^{+3}+e^{-1}$	−1.51

* The data contained in this table are taken from Latimer and Hildebrand, 1940, pp. 474–478; and Latimer, 1938, pp. 294–301.
† The oxidation potentials are for unit activities at 25° C. (298° K.) and 1 atm. of pressure.

there listed (effective unit concentrations, 25° C., and 1 atm. of pressure) when the other half of the oxidation-reduction pair is ferric to ferrous iron. The reaction proceeds in three stages, which are given herewith (for the sake of completeness, sphalerite is used as the initial source of sulfide ion):

$$ZnS + 2Fe^{+3} + 3SO_4^{-2} \rightarrow 2Fe^{+2} + Zn^{+2} + 3SO_4^{-2} + S\,, \qquad (3a)$$

$$S + 4Fe^{+3} + 6SO_4^{-2} + 3H_2O \rightarrow 4Fe^{+2} + 4SO_4^{-2} + 6H^{+1} + 2SO_4^{-2} + SO_3^{-2}\,, \qquad (3b)$$

$$2H^{+1} + SO_3^{-2} + 2Fe^{+3} + 3SO_4^{-2} + H_2O \rightarrow 2Fe^{+2} + 4H^{+1} + 4SO_4^{-2}\,. \qquad (3c)$$

By adding algebraically the oxidation potentials of the two electronic reactions involved in each of these equations, the net emf in each can be determined. Under standard conditions in acid solutions, these emf are:

$$-0.14 - (-0.77) = +0.63 \text{ volt}\,, \qquad (3a')$$

$$-0.45 - (-0.77) = +0.32 \text{ volt}\,, \qquad (3b')$$

$$-0.20 - (-0.77) = +0.57 \text{ volt}\,. \qquad (3c')$$

Because each product is a positive voltage, the reaction will go in the direction indicated in each instance. This obviously does not prove that these reactions will go to the right under all conditions. In certain supergene solutions of low pH and relatively low iron concentration the reaction of equation (*3b*) at least might be reversed, but even this is unlikely. This discussion does show, however, that the reactions of the last three equations are possible and does nothing to demonstrate that they do not often occur.

In several of the equations to be taken up shortly, the oxidation of the sulfide to the sulfate ion is not accomplished by the reduction of ferric to ferrous iron alone. Rather, the process is carried forward in part by one or more of the following reductions acting in conjunction with that of ferric ion: cupric ion to cuprous, cupric to native copper, cuprous to copper, and silver ion to native silver. It is assumed that the emf of the various half-reactions remains the same in such mixed cells, unless that mixing also entails a change in effective concentrations. It is also believed that the tendency of one reaction to go in one direction may be more than counterbalanced by that of another to go in the opposite direction. For example, the emf of the electronic reaction of ferrous to ferric ion is +0.77 volt, whereas that of copper to cupric ion is −0.345 volt. As was shown by the calculations based on equation (*3b*), the reduction of ferric to ferrous iron can drive forward the oxidation of sulfur to sulfite ion. It is equally apparent from equations (*3d*) and (*3e*) and the calculations which follow them that the reduction of cupric ion to native copper does not produce a sufficient emf to drive the second and third stages of the sulfur oxidation forward. This is particularly apparent if it is noted from table 2 that the reduction of cupric ion to native copper actually is carried out in two stages—cupric to cuprous and cuprous to copper. The oxidation potential of the half-reaction converting cuprous to cupric ion is −0.17 volt, which is higher than the potentials for either the second or the third stage of the sulfur oxidation in acid solutions, as shown in the following equations:

$$S + 4Cu^{+2} + 2SO_4^{-2} + 3H_2O \rightarrow 4Cu^{+1} + 6H^{+1} + SO_3^{-2} + 2SO_4^{-2}, \qquad (3d)$$
$$\text{emf} = -0.45 - (-0.17) = -0.28 \text{ volt};$$

$$H_2SO_3 + H_2O + 2Cu^{+2} + 2SO_4^{-2} \rightarrow 2Cu^{+1} + 3SO_4^{-2} + 4H^{+1}, \qquad (3e)$$
$$\text{emf} = -0.20 - (-0.17) = -0.03 \text{ volt}.$$

Equations (*3d*) and (*3e*) show that, under standard conditions, the reduction of cupric ion would never achieve the first stage (reduction to cuprous ion). Because of this, the fact that the emf of the second stage of the copper reduction is less than any of the emf's in the sulfur oxidation has no practical importance because no cuprous ion would be formed to permit the cuprous-copper half-reaction to come into being.

Because the ferric ion reduction, however, proceeds as shown in equation (*3b*) with a net emf of +0.32 volt, the end-result is (when both ferric and cupric ions are present) a net positive emf in favor of both the second and the third stage of the sulfur oxidation under standard conditions. This emf will be only 0.04 volt in the second step in sulfur oxidation but will rise to 0.44 volt in the third. Even though conditions

deviate from standard, as long as the concentrations of ferric and cupric ions are nearly equal or the latter are in the minority, the greater emf of the ferric ion reduction will overcome the weaker force of that of copper to cupric ion.

If it is remembered that the solutions which carry out both supergene and hypogene replacements almost certainly do not contain their various components in unit effective concentrations, it is apparent that the voltages given in the preceding paragraph are not immutable. With any change in the effective concentration of any of the components entering into the oxidation-reduction reaction in question, there will be a change in the reaction's net emf. Of the ions taking part in the reactions of the oxidation of sulfur, the one whose change most greatly varies the emf is the hydrogen. This can be seen from the Nernst equation given below. It is unlikely that supergene solutions, much less hypogene, will have an effective concentration of hydrogen ion greater than 10^{-3} (pH = 3). Accepting 10^{-3} as the effective concentration of the hydrogen ion in the half-reaction for the second stage of sulfide ion oxidation (the activities of the other components remaining at unity), a new oxidation potential for this half-reaction can be determined, as follows:

$$E = E^{\circ}_{25^{\circ}} - \frac{RT}{nF} \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \qquad \text{(Nernst equation)}$$

$$= -0.45 - \frac{2.303RT}{nF} \log_{10} \frac{a_{SO_3} a_H^4}{a_S a_{H_2O}^3}$$

$$= -0.45 - \frac{0.05915}{4} \log_{10} \frac{1\,(10^{-3})^4}{1 \times 1}$$

$$= -0.45 - 0.0148 \log_{10} 10^{-12}$$

$$= -0.45 + 0.18 = -0.27 \text{ volt}.$$

Thus, in acid solutions of the maximum acidity to be expected under even supergene conditions, the oxidation potential of the half-reaction in question (and in any other in which the hydrogen ion is one of the reducible substances produced) is increased over that obtained with a hydrogen-ion activity of unity. In this particular case the oxidation potential is still less than that for the oxidation of cuprous to cupric ion. This means that the reaction of equation (3*d*) would not go forward unless again aided by ferric ion reduction. The amount of help required from ferric ion is, however, much less because the deficit in equation (3*d*) is, with the substitution of the new sulfur-sulfite potential, only 0.10 volt. This same change in hydrogen-ion concentration would also affect the sulfite-sulfate potential, changing it from −0.20 to −0.02 volt.

If the hydrogen-ion concentration were to be lowered even more, to 10^{-5}, for example, the oxidation potential for the sulfur-sulfite half-reaction would be raised to −0.15 volt and that of the sulfite-sulfate to +0.10 volt. Both, then, would be greater than those of either stage in the copper reactions because the change of hydrogen-ion concentration has no effect on the various copper potentials. In strongly acid solutions in which the reduction of cuprous ion to copper or cupric ion to cuprous or na-

tive copper is involved, it may be necessary to appeal to a stronger oxidizing agent than ferric iron to aid the particular copper ion reduction in question. Such an agent might be manganic (Mn^{+3}) ion, which, in its reduction to manganous (Mn^{+2}), has a reduction potential of 1.51 volts.

From this discussion it would seem reasonable that the reduction of cupric to cuprous ion would, in most weakly acid supergene solutions, insure the oxidation of sulfide ion through its three stages to the sexivalent positive sulfur of the sulfate radical. If the replacing solutions were to be alkaline, as they well may be under hypogene conditions, then the oxidation potentials for the sulfur half-reactions would be those for alkaline solutions and would have far higher values. This means that, in alkaline solutions, any half-reaction of an emf less than, say, +0.40 volt would have sufficient emf to drive S^{-2} through the three steps to S^{+6}. This widens the field of choice of oxidizing agents greatly over that which is available for use in supergene environments. It must be emphasized again that it is not claimed that replacing solutions have all ions but the hydrogen at unit effective concentrations, even though, for simplicity, they have been allowed to remain so in the calculations just made. But it is claimed that the Nernst equation shows that a change in hydrogen-ion concentration will have a far greater effect on the oxidation potential of the second and third stages of sulfide ion oxidation than will changes in the effective concentrations of the other components. This is true because the power to which the hydrogen-ion concentration is raised in that equation is higher than for any other constituent. This idea can be made more general in application by saying that a change in the effective concentration of the hydrogen ion will have a greater effect than will a change in concentration of any other ion on the value of the oxidation potential of any half-reaction in which the number of hydrogen ions formed by it is greater than the number of ions of any other reducible substance produced.

HOST IN EXCESS

In the replacement reaction (sphalerite by argentite) which has just been discussed, it was necessary to remove and oxidize some sulfide ions from the host because an equal volume of the guest could not utilize them. The reverse of this situation would obtain if the volume of the host being replaced held less sulfur than would be required by an equal volume of guest. This type of metasomatism is illustrated by the replacement of sphalerite by covellite.

$$ZnS + Cu^{+2} + SO_4^{-2} \rightarrow CuS + Zn^{+2} + SO_4^{-2}. \qquad (4a)$$

The actual space occupied by 1 formula unit (molecule) of sphalerite is 39.37 Å^3 (see table 1), while that taken up by 1 molecule of covellite is 34.24 Å^3. If replacement of sphalerite by covellite occurred exactly as represented by equation (*4a*), there would be a loss of nearly 15 per cent in volume during the process. Because such a loss in volume does not take place under the conditions of hypogene or supergene metasomatism, it follows that equation (*4a*) must be modified to equate not only molecular units but unit volumes as well. From the data just given it is quickly seen that the replacement of 1 molecule of sphalerite (Vol. = 39.37 Å^3) by 1 molecule of covellite (Vol. = 34.24 Å^3) would leave a deficit of 5.13 Å^3 of covellite if volume-for-volume relations are to be preserved. These 5.13 Å^3 are almost exactly 15 per cent of

the volume of 1 formula unit of covellite. This means that 1.15 formula units of covellite must be made available for each formula unit of sphalerite replaced if no loss in volume is to occur. To eliminate fractions of molecules, it is necessary to multiply the 1.15 molecules of covellite and the 1 molecule of sphalerite by 20, i.e., 23 molecules of covellite must be provided for each 20 molecules of sphalerite removed. Where, however, are these extra 3 molecules of covellite to be obtained? They cannot be secured by the replacement of zinc atoms from additional sphalerite by cupric ions from the replacing solution because that would further widen the gap between initial and final volumes. There is, it must be emphasized, a lack not merely of cupric ions but of sulfide ions as well, and these sulfide ions must come from the solutions involved and not from the body of the host mineral. In short, it is not sufficient to introduce three additional cupric ions from a solution in which they are in balance with some acid radical or ion other than the sulfide. Each of the 3 cupric ions must be, at the time of entry into the host volume, in balance with a sulfide ion, and all 3 molecules must be introduced into the space vacated by the 20 zinc atoms at the same time as are the 20 cupric ions required to balance the 20 sulfide ions inherited from the sphalerite.

The reaction which has just been discussed probably can be seen more clearly if it is expressed in the form of an equation, as it is in equation (5*a*), which follows:

$$\left.\begin{array}{l} 20ZnS + 23Cu^{+2} + 20SO_4^{-2} + 3S^{-2} \rightarrow 23CuS + 20Zn^{+2} + 20SO_4^{-2}, \\ (787.40\ \text{Å}^3) \qquad\qquad\qquad\qquad (787.52\ \text{Å}^3) \end{array}\right\} \quad (5a)$$

Volume difference = 0.02 per cent.

Equation (5*a*), however, indicates that the additional sulfur needed to put the equation on a volume-for-volume basis is transported in the replacing solutions as sulfide ion. If this sulfide ion is presumed to come from hydrogen sulfide, the work of Allen, Crenshaw, and Johnson (1912, p. 172) shows that any solutions containing it must have been essentially lacking in oxygen. If such an environment did not obtain, the hydrogen sulfide would be rapidly oxidized as follows:

$$H_2S + 2O_2 = H_2SO_4 .$$

This hydrogen sulfide also must be in excess over ferric ion, or the iron would be reduced to the ferrous state and all the sulfide ion oxidized in steps (see eqs. [3*a*], [3*b*], and [3*c*]) to the S^{+6} of the sulfate radical. It is doubtful if these requirements could be fulfilled on any appreciable scale above the water table. Below it, however, it seems probable that both conditions could be met in considerable volumes of supergene enriching solutions (Emmons, 1917, pp. 98–99 and 150–152). Granting this, equation (5*a*) can be modified slightly to show the presence of H_2S without affecting the volumetric balance it attained:

$$20ZnS + 23Cu^{+2} + 23SO_4^{-2} + 3H_2S \rightarrow 23CuS + 20Zn^{+2} + 20SO_4^{-2} + 6H^{+1} + 3SO_4^{-2} . \quad (5b)$$

The additional covellite required for volumetric balance, then, is provided by a direct reaction between sulfide ion from the dissociation of hydrogen sulfide and cupric ion, as is shown in equation (4*b*) as follows:

$$Cu^{+2} + SO_4^{-2} + H_2S \rightarrow CuS + 2H^{+1} + SO_4^{-2} . \quad (4b)$$

Equation (5*b*) is equation (4*a*) multiplied by 20 and added to equation (4*b*) multiplied by 3.

Because no oxidation or reduction is involved in equation (5*b*), it is necessary to consider the free-energy relations concerned, to see whether the reaction will go forward. This is easily done by examining the free energies of formation of the products and reactants in the two component equations of equation (5*b*). From Kelley's (1937) and Verhoogen's (1938*a*) calculations of the free energies of formation of metal ions, sulfides, and sulfates (see table 3), it can be determined that both these reactions will go

TABLE 3*

Compound or Ion	Free Energy of Formation in Calories at 298.1° K.	Compound or Ion	Free Energy of Formation in Calories at 298.1° K.
$MnSO_4$	−228,020	CdS	− 33,490
$ZnSO_4$	−208,090	FeS_a	− 23,390
$CdSO_4$	−195,760	PbS	− 22,730
$PbSO_4$	−193,650	CoS	− 21,060
$CoSO_4$	−183,650	Cu_2S	− 20,550
H_2SO_4	−176,540	Fe^{+2}	− 20,240
SO_4^{-2}	−176,540	Co^{+2}	− 13,375
$CuSO_4$	−157,950	CuS	− 11,700
Ag_2SO_4	−146,800	Ag_2S	− 8,680
MoS_2	− 54,190	$H_2S_{(g)}$	− 7,865
Mn^{+2}	− 50,730	$H_2S_{(aq)}$	− 6,490
MnS	− 45,520	Pb^{+2}	− 5,810
FeS_2	− 44,720	HgS	− 3,350 (+above 200°)
ZnS	− 40,370		
Bi_2S_3	− 39,140	Cu^{+2}	+ 15,900
Zn^{+2}	− 35,100		

*The data from which this table was compiled were derived from Kelley (1937) in the main, but values were calculated for a few metal ions not given by him, using the formula given by Verhoogen (1938*a*) as his equation (12).

to the right when carried out separately. The free-energy change in (4*a*) in calories is:

Reactants		Products	
ZnS	−40,370	CuS	−11,700
Cu^{+2}	+15,900	Zn^{+2}	−35,100
	−24,470		−46,800
			−24,470
			−22,330

In equation (4*b*) the change in calories is:

Reactants		Products	
Cu^{+2}	+15,900	CuS	−11,700
$H_2S_{(aq)}$	− 6,490		+ 9,410
	+ 9,410		−21,110

Thus not only is the free-energy change such that the reactions will tend to go as written, but also it is nearly the same in each of the two cases. It seems, therefore, quite likely that both reactions could be carried out simultaneously in supergene solutions, as is suggested in equation (5*b*).

The source of the necessary hydrogen sulfide used in reactions such as equation (5*b*) probably is the reaction of sulfuric acid (or rather the hydrogen ion produced by the ionization of sulfuric acid) with such sulfides as pyrrhotite, sphalerite, alabandite, and galena. From a consideration of the free energies involved, it would be doubtful whether galena would contribute any hydrogen sulfide, except that the products probably include $PbSO_{4(s)}$ instead of Pb^{+2} and SO_4^{-2}. Wells, quoted by Emmons (1917, pp. 119–121), found that some hydrogen sulfide was produced when galena was treated with dilute sulfuric acid, but only about one-fourth as much as was formed when sphalerite was similarly attacked. This replacement of lead by hydrogen is consistent with the position of lead in the electromotive series and with free-energy change, as can be seen in the following equation:

$$PbS + 2H^{+1} + SO_4^{-2} \rightarrow H_2S + PbSO_4 .$$

Reactants		Products	
PbS	− 22,730 cal.	$PbSO_4$	−193,650 cal.
H_2SO_4	−176,540	H_2S	− 6,490
	−199,270		−200,140
			−199,270
			− 870

As can be seen from table 3, two of the other three sulfides (MnS and ZnS) have free energies of formation low enough to permit the formation of H_2S when they are brought into contact with dilute sulfuric acid. Pyrrhotite is of particular interest because it is known that it produces far more hydrogen sulfide in this manner than any other sulfide does. A quantitative examination of that reaction, however, cannot be made, since nothing is known about its free energy of formation. If it is assumed that its free energy is about that of ferrous sulfide, then the large production of H_2S can be explained. The reaction is as follows:

$$FeS_a + 2H^{+1} + SO_4^{-2} \rightarrow H_2S + Fe^{+2} + SO_4^{-2} .$$

Reactants		Products	
FeS_a	−23,390 cal.	Fe^{+2}	−20,240 cal.
		H_2S	− 6,490
			−26,730
			−23,390
			− 3,340

Pyrite is a special case, since its very low free energy of formation, much lower than would be expected, prevents it from reacting with sulfuric acid as does pyrrhotite.

It must be understood that the values used for the free energies of formation are exact only for 1 atm. of pressure and 298.1° K. Under any other conditions the values here used are not correct but probably indicate the general order of magnitude, in any environment, of the free energies of formation of the various compounds and ions considered. A comprehensive study of the problem is made by Verhoogen (1938*a* and *b*).

As an alternate scheme to that just proposed, it is suggested that there is a possibility that the sulfur is brought to the scene of the metasomatism as the sexivalent positive sulfur of the sulfate radical and there reduced to S^{-2} by the action of some naturally occurring reducing agent (of higher oxidation potential than that of any of the three half-reactions pertaining to the reduction of S^{+6}). From table 2, it can be seen that such a reducing agent must have an oxidation potential somewhat greater than −0.14 volt, preferably 0.00 volt or higher. A reducing agent which meets these requirements and which also is likely to be found in supergene enriching solutions is not easily discovered in the usual oxidation-reduction tables. The best suggestion that I have been able to find is the oxidation of one or more of the following ions: Cr^{+2} to Cr^{+3}, V^{+2} to V^{+3}, Mo^{+3} to Mo^{+5}, Ti^{+2} to Ti^{+3}, Cd^{+1} to Cd^{+2}, or any similar reaction for which a standard potential can be discovered. Since cadmium is to be found associated with most sphalerite, it is being used to write a possible equation, even though it is realized that the rather uncommon Cd^{+1} ion probably seldom is available in sufficient quantity to do the job. The possible equation is:

$$\left.\begin{aligned} 20ZnS + 23Cu^{+2} + 23SO_4^{-2} + 24Cd^{+1} + 12SO_4^{-2} + 24H^{+1} + 12SO_4^{-2} \rightarrow \\ 23CuS + 20Zn^{+2} + 20SO_4^{-2} + 24Cd^{+2} + 24SO_4^{-2} + 12H_2O\,. \end{aligned}\right\} (5c)$$

If the rather unusual Cd_2^{+2} ion is not thought likely to be present or, if present, to be in sufficient abundance to accomplish the S^{+6} reduction, it may be substituted for, or supplemented by, ions of one or more metals of similar chemical properties and oxidation potentials, as follows:

$$\left.\begin{aligned} 20ZnS + 23Cu^{+2} + 23SO_4^{-2} + 24Cr^{+2} + 24SO_4^{-2} + 24H^{+1} + 12SO_4^{-2} \rightarrow \\ 23CuS + 20Zn^{+2} + 20SO_4^{-2} + 24Cr^{+3} + 36SO_4^{-2} + 12H_2O\,. \end{aligned}\right\} (5d)$$

In addition to the suitable metals, potentials for the oxidation of whose ions are given in table 2, others which should be satisfactory include tungsten, zirconium, and tantalum. The potentials for the half-reactions of the ions of these metals are not available but should be within the range in potentials from the Cd_2^{+2} oxidation to that of $Mo^{+3}(r)$.

It is chemically axiomatic that the ferric-sulfide ion reduction oxidation of equations (*2a*) and (*2b*), on the one hand, and the hydrogen sulfide precipitation of equation (*5b*) or the sulfate ion reduction used in equations (*5c*) and (*5d*), on the other, cannot go on simultaneously in the same system. A sulfide ion cannot be oxidized under the same conditions as those under which a sulfate ion is being reduced. Nor can the precipitation of sulfides by H_2S go on in the presence of ferric ion. In the open systems which exist in ground waters in contact with ore bodies, however, it is possible that, at different times, both these types of mutually exclusive reactions may take place in the same area or that, at the same time, both may be going forward in two different places not necessarily removed from each other by any great distance.

If the reasoning of the last paragraph is correct, it follows that reactions of the type of equations (*2a*) and (*2b*) cannot occur in supergene processes at the same time and in the same place as those like equations (*5b*), (*5c*), and (*5d*). It also seems apparent that in the rare simultaneous supergene replacements of one mineral by two or more, volume adjustments must be made either through the deposition of the

replacing minerals in proper proportions to achieve volumetric balance or through the help of one of the two general types of supplementary reactions, but not through the aid of both. For example, a molecularly balanced equation can be written for the replacement of sphalerite by covellite and argentite, unlikely as that would be under supergene conditions, using any desired ratio between the replacing minerals. But if such an equation is to be balanced in relation to volume as well, the ratio of covellite to argentite must be 3 to 1, and even then the volume difference is over 2 per cent. A volume difference of about 0.5 per cent can be attained (see eq. [6]) if 7 molecules of sphalerite are used, 3 being replaced by covellite, 3 by argentite, and 1 being dissolved by the action of ferric ion to oxidize the sulfur of one sphalerite molecule to sulfate ion, as follows:

$$\left.\begin{array}{l} 7ZnS + 6Ag^{+1} + 3Cu^{+2} + 8Fe^{+3} + 18SO_4^{-2} + 4H_2O \rightarrow \\ (275.59\ \text{Å}^3) \\ \qquad\qquad 3Ag_2S \ + \ 3CuS + 7Zn^{+2} + 8Fe^{+2} + 8H^{+1} + 19SO_4^{-2}, \\ \qquad\qquad (174.33\ \text{Å}^3)\ (102.72\ \text{Å}^3) \end{array}\right\} (6)$$

Volume difference = 0.53 per cent.

It seems probable that there are definite limits as to the ratios in which any two or more minerals can replace a host, under hypogene as well as supergene conditions. These limits are set, it appears, by the relative volumes of the formula units of the minerals concerned. In some cases volumetric balance may be attained without recourse to the dissolving of additional host or the precipitation of extra amounts of one or more of the guests. It seems likely, however, that one or the other of the two processes (additional solution or deposition) must be invoked in most cases of such reactions. Both cannot take place at the same time and in the same system.

FURTHER EXAMPLES

Further to illustrate the volumetric and molecular balancing of replacement equations, the following eight reactions have been selected from those which are generally accepted as occurring during supergene metasomatism.[5] From the data in table 1 it appears that some of these reactions come near enough to volumetric balance not to need any modification, but the others require a good deal.

$$CuFeS_2 + Cu^{+2} + SO_4^{-2} \rightarrow 2CuS + Fe^{+2} + SO_4^{-2}, \quad (7)$$

$$5FeS_2 + 14Cu^{+2} + 14SO_4^{-2} + 12H_2O \rightarrow 7Cu_2S + 5Fe^{+2} + 5SO_4^{-2} + 24H^{+1} + 12SO_4^{-2}, \quad (8a)$$

$$4FeS_2 + 7Cu^{+2} + 7SO_4^{-2} + 4H_2O \rightarrow 7CuS + 4Fe^{+2} + 4SO_4^{-2} + 8H^{+1} + 4SO_4^{-2}, \quad (9a)$$

$$Cu_5FeS_4 + Cu^{+2} + SO_4^{-2} \rightarrow 2Cu_2S + 2CuS + Fe^{+2} + SO_4^{-2}, \quad (10)$$

$$5CuS + 3Cu^{+2} + 3SO_4^{-2} + 4H_2O \rightarrow 4Cu_2S + 8H^{+1} + 4SO_4^{-2}, \quad (11a)$$

$$Cu_2S + 4Ag^{+1} + 2SO_4^{-2} \rightarrow 2Cu^{+2} + 2SO_4^{-2} + Ag_2S + 2Ag, \quad (12a)$$

$$Cu_2S + 6Fe^{+3} + 9SO_4^{-2} + 4H_2O \rightarrow 2Cu + 6Fe^{+2} + 6SO_4^{-2} + 8H^{+1} + 4SO_4^{-2}, \quad (13a)$$

$$PbS + 4O \rightarrow PbSO_4. \quad (14a)$$

[5] Eqs. (7)–(11a) have been taken from Bateman (1942, p. 277), (12) from Lindgren (1905, p. 101), (13a) from Emmons (1917, p. 258), and (14a) from Anderson (1930, p. 529).

Inspection of the equations just given and the unit volumes of the host and guest minerals show that equations (7) and (10) come fairly close to volumetric balance without any change in proportions or reactants. Equation (7) balances within 3.1 per cent and equation (10) within 2.2 per cent; although these deviations are somewhat higher than the limit of 1 to 2 parts in 100 for such variations, they are allowed to stand without any rearrangement.

Equations (8*a*), (9*a*), (11*a*), (12*a*), (13*a*), and (14*a*), however, require considerable change to put them in both volumetric and molecular balance. In equations (8*a*) and (9*a*) it is necessary to remove more pyrite than the reaction given will permit. This means that another reaction which dissolves pyrite and leaves no solid products behind must go on concurrently with those of equations (8*a*) and (9*a*). The reactions suggested by Stokes (1901, p. 15) and given as equations (15*a*) and (16) probably will do the job. Equation (15*a*) is quite similar to equation (3*a*), and equation (16) is the total of equations (3*b*) and (3*c*) multiplied by 2.

$$FeS_2 + 2Fe^{+3} + 3SO_4^{-2} \rightarrow 3Fe^{+2} + 3SO_4^{-2} + 2S\,, \qquad (15a)$$

$$2S + 12Fe^{+3} + 18SO_4^{-2} + 8H_2O \rightarrow 12Fe^{+2} + 12SO_4^{-2} + 16H^{+1} + 8SO_4^{-2}\,. \qquad (16)$$

If these two reactions are combined with equations (8*a*) and (9*a*), respectively, with the necessary pyrite added to achieve volumetric balance, the following equations, (8*b*) and (9*b*), result:

$$\left.\begin{array}{l} 8FeS_2 + 42Fe^{+3} + 63SO_4^{-2} + 14Cu^{+2} + 14SO_4^{-2} + 36H_2O \rightarrow \\ \text{(315.84 Å}^3\text{)} \\ \qquad\qquad 7Cu_2S + 50Fe^{+2} + 50SO_4^{-2} + 72H^{+1} + 36SO_4^{-2}\,, \\ \qquad\qquad \text{(318.78 Å}^3\text{)} \end{array}\right\} (8b)$$

Volume difference = 0.92 per cent ;

$$\left.\begin{array}{l} 6FeS_2 + 28Fe^{+3} + 42SO_4^{-2} + 7Cu^{+2} + 7SO_4^{-2} + 20H_2O \rightarrow \\ \text{(236.88 Å}^3\text{)} \\ \qquad\qquad 7CuS + 34Fe^{+2} + 34SO_4^{-2} + 40H^{+1} + 20SO_4^{-2}\,, \\ \qquad\qquad \text{(239.68 Å}^3\text{)} \end{array}\right\} (9b)$$

Volume difference = 1.16 per cent .

The modification of equation (11*a*) presents a somewhat different problem because here it is necessary to remove more covellite than the reaction given will permit, to provide room for the chalcocite formed. To accomplish this, a second reaction must go on at the same time as that of equation (11*a*) to remove the excess covellite without leaving any solid products behind. A slight change in equation (15*a*) should take care of this, however, while equation (16) must be halved. This change in equation (15*a*) is given in equation (15*b*):

$$CuS + 2Fe^{+3} + 3SO_4^{-2} \rightarrow Cu^{+2} + SO_4^{-2} + 2Fe^{+2} + 2SO_4^{-2} + S\,. \qquad (15b)$$

When equations (11*a*), (15*b*), and (16) are combined, the result is:

$$\left.\begin{array}{l} 21CuS + 12Cu^{+2} + 12SO_4^{-2} + 8Fe^{+3} + 12SO_4^{-2} + 20H_2O \rightarrow \\ \text{(719.04 Å}^3\text{)} \\ \qquad 16Cu_2S + Cu^{+2} + SO_4^{-2} + 8Fe^{+2} + 8SO_4^{-2} + 40H^{+1} + 20SO_4^{-2}\,, \\ \qquad \text{(728.64 Å}^3\text{)} \end{array}\right\} \quad (11b)$$

Volume difference = 1.32 per cent.

To adapt equation (12*a*) requires a further change in equation (15*a*) and its combination with equation (16), which again it is necessary to halve:

$$Cu_2S + 4Fe^{+3} + 6SO_4^{-2} \rightarrow 2Cu^{+2} + 2SO_4^{-2} + 4Fe^{+2} + 4SO_4^{-2} + S\,. \quad (15c)$$

In equation (15*c*), in addition to oxidizing the sulfide ion, ferric ion also is called upon to oxidize cuprous ion as well. From table 2 it can be seen that the necessary electronic reactions are such that the reaction will go with an emf of +0.60 volt:

$$\left.\begin{array}{l} 2Cu_2S + 4Ag^{+1} + 2SO_4^{-2} + 10Fe^{+3} + 15SO_4^{-2} + 4H_2O \rightarrow \\ \text{(91.08 Å}^3\text{)} \\ \qquad Ag_2S + 2Ag + 4Cu^{+2} + 4SO_4^{-2} + 10Fe^{+2} + 10SO_4^{-2} + 8H^{+1} + 4SO_4^{-2}\,, \\ \qquad \text{(58.11 Å}^3\text{)} \quad \text{(33.90 Å}^3\text{)} \end{array}\right\} \quad (12b)$$

Volume difference = 1.01 per cent.

In equation (12*b*) ferric ion is assisted in its oxidation of the sulfide ion by the reduction of both cuprous and silver ions to the native metals. From table 2 it is apparent that the emf of the half-reaction involving silver is even less than that involving ferrous ion. Therefore, silver ion can aid in all three stages of sulfide ion oxidation to an even greater extent than can ferric. The emf of the half-reaction containing the cuprous ion, although greater than that with ferrous ion, still is less than that of the second stage in the oxidation of sulfide ion and, therefore, will aid in all stages of the oxidation.

The rearrangement of equation (13*a*) is somewhat more complicated than is that of those from equations (7) through (12*a*). It resembles equation (4*a*) in that, if molecularly balanced, the volume of solid reactant is larger than that of solid product. It differs from equation (4*a*), however, in that the reduction needed for volumetric balance is not that of sulfate to sulfide ion but that of cupric ion to native copper. The reduction of cuprous ion from the chalcocite to copper must also be taken care of, as well as the oxidation of the sulfide ion of the chalcocite to sulfate. It has already been pointed out in the discussion of equation (12*b*) that the reduction of cuprous ion to native copper can aid in all stages of the oxidation of sulfide ion. This is not true of the reduction of cupric ion to native copper, however, because that half-reaction has an emf of −0.345 volt, which is greater than that for the second stage of sulfide oxidation. Under standard conditions, therefore, the reduction of cupric ion to native copper would aid only in the first and third stages of the oxidation and would, presumably, oppose the reducing action of ferric ion in the second. If the cupric ion reduction took place in stages, from cupric to cuprous and cuprous to native copper, as it probably does, the relatively high oxidation potential of the first stage of copper reduction would prevent its aiding in both the second and the third stages of sulfide oxidation.

The second stage of reduction (cuprous to copper) would create an emf sufficient to take part in all stages of the oxidation. The initial modification of equation (13*a*) on this basis is as follows:

$$\left.\begin{aligned} Cu_2S + 2Cu^{+2} + 2SO_4^{-2} + 2Fe^{+3} + 3SO_4^{-2} + 4H_2O \rightarrow \\ 4Cu + 2Fe^{+2} + 2SO_4^{-2} + 8H^{+1} + 4SO_4^{-2}\,. \end{aligned}\right\} \quad (13b)$$

Equation (13*b*), although in molecular and electrical balance, still is unbalanced volumetrically by about 3 per cent. This unbalance can be largely removed by combining equation (13*b*), multiplied by 12, with equation (13*a*), taken only once. This combination gives an exact molecular and electrical balance and is within less than 1 per cent of being volumetrically balanced, as can be seen from equation (13*c*):

$$\left.\begin{aligned} 13Cu_2S + 24Cu^{+2} + 24SO_4^{-2} + 30Fe^{+3} + 45SO_4^{-2} + 52H_2O \rightarrow \\ (592.02\ Å^3) \\ 50Cu + 30Fe^{+2} + 30SO_4^{-2} + 104H^{+1} + 52SO_4^{-2}\,, \\ (587.00\ Å^3) \end{aligned}\right\} \quad (13c)$$

Volume difference = 0.85 per cent.

The adaptation of equation (14*a*) to the requirements of volumetric balance is relatively simple, but the explanation of why one-third of the lead sulfate formed is removed in solution is not:

$$\left.\begin{aligned} 3PbS + 12O \rightarrow 2PbSO_4 + Pb^{+2} + SO_4^{-2}\,, \\ (156.39\ Å^3) \qquad (156.96\ Å^3) \end{aligned}\right\} \quad (14b)$$

Volume difference = 0.36 per cent.

SULFIDE AND SULFOSALT REPLACEMENTS—HYPOGENE CONDITIONS

GENERAL

The writing of equations for the reactions of hypogene replacements is a somewhat different and more difficult task than for those of the supergene zone. It is possible, in the latter type of reactions, to put in the equation what well may be all the essential constituents of the reaction, both those in the solid state and those in solution. Enough is known of the chemistry of supergene replacements to do this without great possibility of error. Such completeness is not, however, to be attained in the equational expression of hypogene metasomatism. There is too much uncertainty as to the manner in which the essential and additional ions needed for the reaction are brought to the scene. There is even less knowledge of those ions which are in chemical balance with those which are definitely present in the replacing solutions but which leave no trace of their presence in the replacement minerals. It is beyond the scope of this paper, for example, to debate the merits of colloidal versus complex ion transfer. It is apparent, as well, that complete equations for hypogene replacements cannot be written until that controversy is settled and more is known of the actual composition of, as well as manner of transportation in, the ore-forming fluid. Nevertheless, the possibility remains that skeleton equations, expressing the basic changes which take place, can be written for hypogene replacement reactions.

In completely balanced supergene equations it is possible to determine whether extra replacing mineral must be formed from the components of the ore solutions or additional amounts of the replaced mineral dissolved over the quantities required for simple molecular balance. This is not true of their hypogene counterparts, however, because simple molecularly balanced equations are not possible with the limited data at hand. All that it is possible to do is, by division of one formula unit volume by the other (or others), to determine the number of molecules of guest needed to equal volumetrically a definite number of host molecules. If the correct molecular quantities of the two or more minerals are set forth on opposite sides of an equation, it is immediately apparent that certain components must be added on both sides of the equation. Those on the left are the additional ions needed, over those furnished by the host, to create the guest. Those on the right are those present in the host but not needed in the formation of the guest.

The problem of addition and subtraction of metal ions only is negligible. But, if sulfur is involved, its addition or subtraction is less easily explained. If more sulfide ion is furnished by the host than can be used in the guest, it seems probable that the excess sulfide ion must be oxidized to sulfate for ready removal from the site of the metasomatism. If, on the other hand, less sulfur ion is provided by the host than is needed by the guest, sulfide ion must be supplied from the ore-forming fluid. The mechanism for the production of the requisite amount of sulfide ion is highly debatable. It may come from sulfide ion carried in solution in balance with a free cation, from the dissociation of a metal-sulfur complex ion, or from a colloidal dispersion of metal sulfides. So far as this study is concerned, this supplementary sulfide ion will be assumed to be available when needed as sulfide ion, and no attempt will be made to say how or in what state it reached the point at which it combines with the ions of the host to form the guest. Finally, there are rare cases, such as are indicated by equations (17) and (23), in which sulfide ion is present in the host in the exact quantities needed by the guest. Such happy coincidences are, unfortunately, rare.

Thus in hypogene, as in supergene, replacements there are three general types of molecularly and volumetrically balanced equations: (1) those in which more sulfide ion is provided by the guest than the host can use, which necessitates oxidation and removal in solution of the unwanted sulfide; (2) those in which less sulfide ion is furnished by the host than is requisite to the formation of the guest, which requires the addition of the needed sulfide ion from the solutions; and (3) those in which sulfide ion is present in the host in exactly the amounts which are called for by the guest.

EXAMPLES

The different methods of approach to the balancing of these three types of equations are shown in equations (17)–(26), inclusive, which follow. They were selected to show as wide a variety of hypogene replacements as can be managed from such a small number of examples. They show what can be done to balance such reactions as to both weight and volume.

$$\left.\begin{array}{l} 11PbS + 8Ag^{+1} + 8Cu^{+1} + 2Sb^{+3} \rightarrow Ag_8Cu_8Sb_2S_{11} + 11Pb^{+2}, \\ (573.43\ \text{Å}^3) \qquad\qquad\qquad\qquad (582.11\ \text{Å}^3) \end{array}\right\} \quad (17)$$

Volume difference = 1.47 per cent.

It is quite possible that the copper in the solution accomplishing the replacement of galena by polybasite is in the cupric state and is reduced to the cuprous during precipitation, but there are no data on which to base such a conclusion except the relative instability of the cuprous ion vis-à-vis the cupric:

$$\left.\begin{array}{l} 15ZnS + 4Pb^{+2} + 8Fe^{+3} + 6Sb^{+3} + 4H_2O \rightarrow Pb_4FeSb_6S_{14} + 15Zn^{+2} + SO_4^{-2} \\ (591.00\ \text{Å}^3) \qquad\qquad (582.11\ \text{Å}^3) \\ \qquad\qquad + 7Fe^{+2} + 8H^{+1}, \end{array}\right\} (18)$$

Volume difference = 1.11 per cent.

In this replacement of sphalerite by jamesonite, the presence of an additional molecule of sphalerite, above that required for molecular balance, necessitates the presence in the solution of iron in the ferric state to convert the sulfide ion to sulfate:

$$\left.\begin{array}{l} 8CuFeS_2 + 6Cu^{+2} + 7Sn^{+2} + 12S^{-2} \rightarrow 7Cu_2FeSnS_4 + Fe^{+2}, \\ (565.60\ \text{Å}^3) \qquad\qquad (559.51\ \text{Å}^3) \end{array}\right\} (19)$$

Volume difference = 1.08 per cent.

It will be noted in this metasomatism of chalcopyrite by stannite that the conversion of the cupric copper to cuprous is assumed to be accomplished by the oxidation of the stannous ion from the solution. From table 2 it can be seen that this reaction will go in the direction indicated but slowly because the net emf will be but +0.02 volt under standard conditions.

$$\left.\begin{array}{l} Cu_{12}Sb_4S_{13} + 14Fe^{+3} + 4Pb^{+2} + 4H_2O \rightarrow 4PbCuSbS_3 + 8Cu^{+2} \\ (551.19\ \text{Å}^3) \qquad\qquad (543.00\ \text{Å}^3) \\ \qquad\qquad + 14Fe^{+2} + SO_4^{-2} + 8H^{+1}, \end{array}\right\} (20)$$

Volume difference = 1.47 per cent.

This replacement of tetrahedrite by bournonite requires the oxidation of one ion of sulfur to the sexivalent sulfur of the sulfate ion, and the reduction of ferric to ferrous ion is used as the mechanism to achieve this. There is no reason why this reaction should not go forward as easily under hypogene as under supergene conditions, and, as has been pointed out on page 528, there are several reasons why it may proceed with a greater net emf:

$$\left.\begin{array}{l} 4Cu_3AsS_4 + Cu^{+2} + 2Fe^{+3} + 4H_2O \rightarrow Cu_{12}As_4S_{13} + CuFeS_2 + Fe^{+2} \\ (593.26\ \text{Å}^3) \qquad\qquad (529.03\ \text{Å}^3) \quad (70.70\ \text{Å}^3) \\ \qquad\qquad + SO_4^{-2} + 8H^{+1}, \end{array}\right\} (21)$$

Volume difference = 1.06 per cent.

Equation (21) expresses the essential facts of the replacement of enargite by tennantite and chalcopyrite if the proportions of the latter two minerals to each other are correct, as their volume relations would seem to indicate. As written, the equation is balanced whether the arsenic of the enargite is considered to be tervalent or quinquevalent. The oxidation-reduction reactions taking place would be quite different, depending on the valence used, and both possibilities must be considered.

If the arsenic is As^{+5}, then not only must 1 sulfide ion (which the host contains in excess of the requirements of the guests) be oxidized to sexivalent positive sulfur,

but 4 arsenic ions must be reduced to As^{+3}. In addition, 2 cuprous ions from the enargite must be oxidized to cupric copper. The latter oxidation can be accomplished by the simultaneous reduction of 2 ferric ions to the ferrous state and need concern us no further. The oxidation reduction of S^{-2} and As^{+5}, respectively, might be mutually accomplished if the emf's of the half-reactions taking place bear the proper voltage relations to one another, since the total loss and gain of electrons is equal. Unfortunately, I have been unable to find any published oxidation potentials for half-reactions which could, conceivably, be involved, such as,

$$As^{+3} \rightarrow As^{+5} + 2e^{-1}$$

or

$$2S^{-2} + As_2S_3 \rightarrow As_2S_5 + 2e^{-1}.$$

Nor have I been able to find the necessary data to permit approximate calculations of such potentials. For the reaction to go in the direction indicated in equation (21), however, the value of the arsenic half-reaction must be, under standard conditions, less than +0.48 volt, which is the lowest voltage produced by any of the half-reactions in the oxidation of S^{-2} to S^{+6} of the sulfate radical in the alkaline solutions which probably obtain under hypogene conditions.

If, on the other hand, the arsenic is As^{+3} in the enargite, the oxidation-reduction relations are quite different and must be considered in detail. One sulfide ion must be oxidized to sexivalent positive sulfur. As the reaction here is written, 6 of the 8 electrons removed from that sulfide ion are taken up by the reduction of an equal number of cupric to cuprous ions. The 2 remaining electrons are added to the 2 ferric ions, converting them to ferrous. If this reaction were attempted under the standard conditions at which the oxidation potentials in table 2 were determined, it almost certainly would not proceed as shown. The emf of the cuprous-cupric half-reaction is a −0.17 volt, while that of the second stage of the sulfide ion oxidation is −0.45 volt. This means that the reaction would tend to go in the opposite direction, with a net emf of +0.28 volt. This result might be avoided in neutral or alkaline solutions, as discussed on pages 528–529, in which the oxidation potential of the sulfur-sulfurous ion half-reaction would be greatly increased. Another possible solution to the problem would be to use another oxidizing agent of a considerably lower oxidation potential than that of the ferrous-ferric ion half-reaction. Such an oxidizing agent could be the reduction of manganic to manganous ion.

Equation (21), for the replacement of enargite by tennantite and chalcopyrite, probably represents only an intermediate stage in a reaction whose final product is chalcopyrite alone. All the original enargite and the subsequently developed tennantite are finally replaced by chalcopyrite. Perry (1933, p. 17) mentions the alteration of enargite to chalcopyrite with the formation of some tennantite, apparently as an intermediate step in the reaction, in the northeastern part of the Butte district. Ultimately, this tennantite, too, probably would have been converted to chalcopyrite, had the flow of solutions continued longer. The equation for the development of chalcopyrite from tennantite is given in equation (22):

$$\left.\begin{array}{l} 2Cu_{12}As_4S_{13} + 20Fe^{+3} + 4S^{-2} \rightarrow 15CuFeS_2 + 9Cu^{+2} + 8As^{+3} + 5Fe^{+2}, \\ (1058.08\ \text{Å}^3) \qquad\qquad (1060.50\ \text{Å}^3) \end{array}\right\} \quad (22)$$

Volume difference = 0.23 per cent.

In this reaction the agent used to oxidize the cuprous copper of the tennantite to the cupric of chalcopyrite is considered to be the ferric to ferrous iron reduction. Table 2 shows that this reaction will be, under standard conditions, driven forward with a net emf of +0.60 volt. As has already been stated, no attempt is made to account for the presence of sulfide ion in the replacing solutions in this reaction or that of equation (26), beyond the general one given on page 538.

The equation for the replacement of bornite by chalcopyrite and chalcocite, which follows, is one of the rare replacements, if it can properly be called such, in which no material is added from solution and none taken away. It well may be that such molecular rearrangements which require no extra ions to be given or taken away by the ore-forming fluid should not be called "replacements" at all, even though they are not recognized as unmixings from solid solution.

$$\left.\begin{array}{rcl} Cu_5FeS_4 & \rightarrow & CuFeS_2 + 2Cu_2S\,, \\ (163.21\ \text{Å}^3) & & (70.70\ \text{Å}^3)\quad (91.08\ \text{Å}^3) \end{array}\right\} \qquad (23)$$

Volume difference = 0.88 per cent.

Although there may be some question as to the propriety of calling this reaction "metasomatic," there is no question about the alternate second stages which usually follow that of equation (23). Two very opposite end-products may be obtained. Either the original bornite is almost entirely replaced by chalcocite, or it is almost completely changed to chalcopyrite. In contact with the average ore-forming fluid, the mixture of chalcopyrite and chalcocite does not appear to be a stable combination, perhaps because of the cupric and cuprous copper contained, respectively, in the two minerals. Of the two possible end-results, the more usual of attainment appears to be for the chalcopyrite formed to be replaced by chalcocite almost as soon as it is formed. Other conditions, however, appear to exist upon occasion which favor chalcopyrite as the more stable mineral, and it is formed not only at the expense of bornite but by the metasomatism of chalcocite as well. Edwards (1947, p. 104) discusses this reaction and gives two equations to explain the change of chalcopyrite to chalcocite. To condense the chemical expression of the reaction, these two equations have been combined so that they deal, after multiplying the first by 5, with comparable amounts of reactants and products; and the following modified equation results:

$$\left.\begin{array}{l} 20CuFeS_2 + 42Cu^{+2} + 10Fe^{+3} + 36H_2O \rightarrow 31Cu_2S + 30Fe^{+2} + 72H^{+1} + 9SO_4^{-2}\,, \\ (1414.00\ \text{Å}^3)\qquad\qquad\qquad\qquad (1411.74\ \text{Å}^3) \end{array}\right\} \qquad (24)$$

Volume difference = 0.16 per cent.

If equation (23) is multiplied by 20 and combined with equation (24), the result is equation (25), as follows:

$$\left.\begin{array}{l} 20Cu_5FeS_4 + 42Cu^{+2} + 10Fe^{+3} + 36H_2O \rightarrow 71Cu_2S + 30Fe^{+2} + 72H^{+1} + 9SO_4^{-2}\,, \\ (3264.20\ \text{Å}^3)\qquad\qquad\qquad\qquad (3233.34\ \text{Å}^3) \end{array}\right\} \qquad (25)$$

Volume difference = 0.09 per cent.

Edwards concludes that about 67.5 per cent of the copper in the chalcocite formed in equation (25) comes from the bornite and about 32.5 per cent is introduced from solu-

tion. From the figures given in the last three equations, the percentages are calculated as 70.42 and 29.58, respectively.

In equation (25) the oxidation of the extra sulfide ions in the bornite is indicated as being the companion reaction to the reduction of cupric to cuprous ion. A glance at table 2 will show that, under standard acid conditions, the second and third stages of the oxidation of sulfide ion to sulfate would not go forward because the oxidation potential of the cuprous-cupric half-reaction is greater than those of the two half-reactions of sulfide oxidation. If any close approximation of standard conditions exists in the ore-forming solutions, a more powerful oxidizing agent than cupric ion, e.g., ferric or manganic ions, would have to be present to drive the oxidation through the second and third stages. If, however, the ore-forming solutions are neutral or alkaline, the oxidation potential of the second and third stages of sulfide ion oxidation will be those for alkaline solutions and will be higher than that of the cuprous-cupric half-reaction, and the reaction probably will go as shown. This point is more fully discussed on page 529.

If we neglect the effectiveness of the oxidizing agent, the conversion of bornite to chalcocite is a relatively simple problem. That of changing bornite to chalcopyrite in more difficult. To maintain equality of volume, the 2 molecules of chalcocite formed in equation (23) must be converted to 1.3 molecules of chalcopyrite. This additional chalcocite is eliminated through the use of Stokes's equations as modified in equations (15*c*) and (16) of this paper. The result is equation (26):

$$\left.\begin{array}{c} 31Cu_2S + 62Fe^{+3} + 9S^{-2} \rightarrow 20CuFeS_2 + 42Cu^{+2} + 42Fe^{+2}, \\ (1411.74\ \text{Å}^3) \qquad\qquad (1414.00\ \text{Å}^3) \end{array}\right\} \quad (26)$$

Volume difference = 0.16 per cent.

Again the ferric to ferrous iron reduction is appealed to as the agent to oxidize the cuprous ion to cupric, as was done in equation (22), for example.

THE REDUCTION OF FERRIC IRON AND ITS IMPLICATIONS

In formulating several of the equations above for hypogene replacement reactions, reduction of ferric to ferrous iron proved necessary to attain electrical balance between reactants and products. This is justified by analogy with the more completely known reactions of supergene enrichment and because of the almost exclusively ferrous nature of the iron found in sulfides and sulfosalts. The presence of many minerals containing substantial amounts of ferric iron in common igneous rocks would indicate a supply of ferric ions in the magma from which these rocks were derived. These ions, once the magma had cooled sufficiently to permit their formation, probably would be available for ejection from the magma chamber at any stage of the crystallization cycle by any mechanism adequate to the task. Granting that the ore-bearing fluid was formed from the magma at some point in that cycle (and before the supply of ferric ions was essentially exhausted, if that point ever is reached), it seems probable that such solutions would contain—along with much else, of course—ferric ion or complex ions of which ferric iron was a part. Yet ferric iron is rarely found in sulfide or sulfosalt minerals of ore deposits. Is it not reasonable, then, to assume that the process of hypogene ore deposition is, among other things, one in which the reduction of ferric to ferrous iron is of common occurrence?

SULFIDE REPLACEMENT OF CARBONATES

Because a common phenomenon in the formation of hypogene mineral deposits is the replacement of calcite or dolomite by ore sulfides, it is desirable to see if there is any difficulty in preserving volume and weight relations in the process. Equation (27) is a simple statement of the obvious initial components and final products of such a replacement:

$$Zn^{+2} + S^{-2} + CaCO_3 \rightarrow ZnS + Ca^{+2} + CO_3^{-2}\,. \qquad (27)$$

This equation expresses merely a change of state and not a true chemical reaction, as the only difference between left- and right-hand components of the system is their transfer from solution to solid and vice versa. What causes the change of state is another matter on which no general agreement has been reached. The actual replacement is, in this case, apparently no more complicated than the diffusion of zinc and sulfide ions into the space initially occupied by the unit cells of calcite and the diffusion out of calcium and carbon and oxygen (or carbonate) ions. The role played by other ions present in the replacing solutions may have been vital in driving the reaction forward, but what those ions may have been and what forces they caused to operate is another matter. They have left no record of their presence in the solid minerals (unless it be in the content of liquid inclusions), and their part in the process is beyond the compass of this study to consider. Equation (27) represents a reaction which does take place, and that is the important thing so far as the balancing of that equation is concerned.

From table 1 it is obvious that equation (27) does not express a volume-for-volume reaction. It requires 1.55 formula unit volumes of sphalerite to replace 1 formula unit volume of calcite. This means that, getting rid of fractions, 31 formula units of sphalerite are required to replace 20 such units of calcite if a volumetric balance is to be achieved. Because the reactants in this equation do not have any ion in common, equation (27) is easily re-written as:

$$\left.\begin{array}{l} 20CaCO_3 + 31Zn^{+2} + 31S^{-2} \rightarrow 31ZnS + 20Ca^{+2} + 20CO_3^{-2}\,, \\ (1220.60\ \text{Å}^3) \qquad\qquad (1220.47\ \text{Å}^3) \end{array}\right\} \qquad (28)$$

Volume difference = 0.01 per cent .

Because there is no chemical reaction here which requires balancing, there is no need to increase the number of components on either side of the equation beyond the requirements of volumetric equality. Were the compound replacing calcite of a larger unit cell volume than 122.06 Å^3, then the number of metasome molecules involved would be less than the number of those of the host; but that is of minor significance. The important fact is that, in a replacement in which host and guest have no common element, molecular balance is not affected by the equating of unit cell volumes.

In this type of replacement the ions diffusing in and out of the crystal lattices are not solely the relatively small metallic ions but also include the quite large oxygen and sulfur ions as well. According to Fairbairn (1943, p, 1314) the sulfur ion (ionic radius = 1.74 Å) is about 1.5 times as large as the oxygen component of the carbon-

ate radical. Its size, however, is small enough in comparison with the packing factors of the minerals involved[6] to permit the postulated diffusion.

NONMETALLIC REPLACEMENT OF CARBONATES

One possible nonmetallic replacement of carbonate is that of calcite by fluorite. It is a relatively simple reaction, shown in equation (29):

$$CaCO_3 + 2H^{+1} + 2F^{-1} \rightarrow CaF_2 + H^{+1} + HCO_3^{-1}, \tag{29}$$

which differs from those that have been taken up so far in that there is no change in the cation which is calcium before, after, and during the metasomatism. The equation is not, however, in volumetric balance because the unit cell of calcite is 122.06 Å^3, while that of fluorite is 161.8. This leads to the conclusion that more calcium and fluorine must be added during the metasomatism than are required by molecular equality in the reaction. Equation (30) indicates one way in which this could be accomplished:

$$\left.\begin{array}{l} 2CaCO_3 + Ca^{+2} + 4H^{+1} + 6F^{-1} \rightarrow 3CaF_2 + 2H^{+1} + 2HCO_3^{-1}, \\ (122.06\ \text{Å}^3) \qquad\qquad (121.38\ \text{Å}^3) \end{array}\right\} \tag{30}$$

Volume difference = 0.56 per cent.

Of course, equation (30) does not explain why calcium fluoride should be deposited from the ore-forming fluid in question or why the reaction of hydrofluoric acid on calcium carbonate should proceed at exactly or very nearly the same rate as does the deposition of fluorite. Nor does it explain why the action of hydrofluoric acid on calcite should be the removal of carbonate ion alone from the cell volumes concerned, without disturbing the calcium ions, which occupy so much smaller a portion of those volumes. An equation is not, however, supposed to do these things. It is an expression of the fact of chemical change, and beyond that it does not go. It would be of far greater value to be able to explain the reasons for the reactions that have been or will be discussed in this paper than to be able to write equations for them. Nevertheless, the explanation of the reactions may be somewhat facilitated, once it is shown that any such reaction can be expressed in a molecularly and volumetrically balanced equation properly indicating at least the correct initial and final products.

OXIDE REPLACEMENT OF SILICATES

If an attempt were to be made completely to balance molecularly and volumetrically the reaction taking place when a sulfide or an oxide replaces a silicate gangue mineral, it probably would fail because of the present lack of knowledge of the chemical characteristics of the ore-forming fluid concerned. Nevertheless, an equation can be written for the replacement, say, of wollastonite (whose formula is considered, for simplicity, to be $CaSiO_3$) by magnetite,

$$Fe^{+2} + 2Fe^{+3} + 4CaSiO_3 \rightarrow Fe_3O_4 + 4SiO_2 + 4Ca^{+2} \tag{31}$$

or

$$3Fe^{+2} + 6Fe^{+3} + 4CaSiO_3 \rightarrow 3Fe_3O_4 + 4Ca^{+2} + 4Si^{+4}, \tag{32}$$

[6] Fairbairn gives a packing index of 4.0 for calcite. Because of the uncertainty of atom size in many sulfides, he gives no data as to the packing indices of sulfides. It appears that the index for sulfur itself lies between 6.5 and 7.0.

in either of the two above incomplete forms, from which much, of necessity, has been omitted.

In the molecularly balanced reaction expressed by equation (31), it is indicated that 260.00 Å^3 of wollastonite are replaced by a total of 223.12 Å^3 of magnetite and silica (73.40 Å^3 from magnetite and 149.72 Å^3 from silica). This leaves a deficit of 36.88 Å^3, which cannot be supplied by silica, because the production of more silica can be attained only by the destruction of further wollastonite. Therefore, the 36.88 Å^3 must be made up by the addition of magnetite (iron and oxygen both) from the solution. There is no more available oxygen to be derived from the wollastonite, once one molecule of magnetite has been formed from it, without breaking down further wollastonite, which would only further increase the volumetric unbalance of the system. Because 36.88 Å^3 of magnetite equals 0.50 formula units of magnetite, it is obvious that $\frac{1}{2}$ formula unit of that mineral must be added to equation (31), in the ionic form on the left-hand side and in the solid state on the right. To eliminate fractions of a molecule, equation (31) must be multiplied by 2 and 1 additional molecule of magnetite must be added, as in equation (33), which follows:

$$\left.\begin{array}{r} 4O^{-2} + 3Fe^{+2} + 6Fe^{+3} + 8CaSiO_3 \rightarrow 3Fe_3O_4 + 8SiO_2 + 8Ca^{+2}, \\ (520.00\ \text{Å}^3)\ (220.20\ \text{Å}^3)(299.44\ \text{Å}^3) \end{array}\right\} \quad (33)$$

Volume difference = 0.07 per cent.

In equation (32), 3 unit volumes of magnetite (220.20 Å^3) appear to have replaced 260.00 Å^3 of wollastonite. The deficiency in magnetite, is therefore, 0.54 formula unit volume, and this much must be added to the solid products from the solution. To eliminate fractions, it is necessary to multiply equation (32) by 20 and add 11 formula units of magnetite to the equation, in the ionic form on the left-hand side and in the solid form on the right, as shown in equation (34):

$$\left.\begin{array}{r} 71Fe^{+2} + 142Fe^{+3} + 80CaSiO_3 + 44O^{-2} \rightarrow 71Fe_3O_4 + 80Ca^{+2} + 80Si^{+4}, \\ (5200.00\ \text{Å}^3) \qquad\qquad (5211.40\ \text{Å}^3) \end{array}\right\} \quad (34)$$

Volume difference = 0.22 per cent.

These four equations—(31) through (34)—say nothing as to the manner in which the ferrous and ferric ions are carried in solution, nor do they supply any information as to the fate of the calcium and silicon ions (if the latter are produced at all) which are removed. It is almost certain that the silicon ion, if it forms, almost immediately becomes part of some acid radical, but the source of the other elements of the radical or what they may be is another problem.

It has been pointed out that the magnetite, above that provided by equations (31) and (32), must be present in the replacing solutions as ferrous, ferric, and oxygen ions or in ionic complexes from which these could easily be derived. The additional magnetite could not be formed by a later reaction of any other iron- and oxygen-bearing compounds because there would almost certainly be a change in volume from such a reaction which it would be simple to detect.

At the same time that the replacement reactions just discussed are taking place, one may also be going forward in immediately adjacent crystals of some other mineral in which oxygen ions must be diffused out. If this is so, a source of oxygen might be

provided without recourse to the solutions carrying the iron ions. It would, however, be remarkable if the number of oxygen atoms not required in one reaction would just balance those needed in another, not to mention the difficulties of solid diffusion across grain boundaries. The need for the transfer of oxygen ions from the attacking solutions in some degree is then almost certain.

If the reaction of equation (33) actually has taken place on a large scale, many contact metamorphic magnetite ore bodies should be high in free quartz. This condition ordinarily does not obtain because the bulk of the iron oxide in such deposits appears to have been emplaced by the replacement of calcite rather than of contact silicates. If the reaction of equation (34) should occur, the formation of free quartz is unlikely; but the silicon ion produced must be removed, probably by the further silication of silicates already present in the immediate area, thus greatly complicating the reaction.

PACKING INDEX AND EASE OF REPLACEMENT

It seems reasonable, as suggested by Fairbairn (1943, p. 1351), that replacement of minerals having a high packing index (high ratio of ion volume to unit cell volume) should be more difficult to accomplish than that of those having a lower one. The replacement of calcite and wollastonite by magnetite or zincite bears this out. In the average contact deposit, the first stage of the process is the formation of a silicate tactite rock which, although high in typical lime-rich silicates, probably contains much recrystallized calcite. It is the consensus (Loughlin and Behre, 1933, p. 48; Schmitt, 1948, p. 4) that the oxides and sulfides which commonly are found in tactites are later than the silicates and possibly formed under less intense conditions. It is also commonly held that such oxides and sulfides usually replace the interstitial calcite in preference to the silicate portion of the rock. A possible explanation of this phenomenon is offered from Fairbairn's suggestion. Calcite has a packing index of 4.0, wollastonite one of 5.2. There is, therefore, over 20 per cent more "open space" in the calcite molecule through which ions can be diffused in and out of the lattice in calcite than in wollastonite. It would be only reasonable, then, in a rock containing a mixture of calcite and wollastonite (or other silicates and carbonates of similar packing relationships) to expect that replacement would be more likely to occur in the calcite.

OXIDE REPLACEMENT OF CARBONATES

The possible equations for such calcite replacements are of interest from the volume-weight standpoint as well. In equations (31) and (32) were given molecularly balanced equations for the replacement of wollastonite by magnetite. Similar equations can be written for a like replacement of calcite:

$$Fe^{+2} + 2Fe^{+3} + 2CaCO_3 \rightarrow Fe_3O_4 + 2Ca^{+2} + C + CO_2\,, \tag{35}$$

$$Fe^{+2} + 2Fe^{+3} + 4CaCO_3 \rightarrow Fe_3O_4 + 4Ca^{+2} + 4CO_2\,. \tag{36}$$

The theoretical basis for equation (35) is supplied by Winchell's work (1911, p. 229) on the formation of graphite. When the data of table 1 are used, these two equations can be volumetrically balanced, as follows:

$$\left.\begin{array}{c} 44O^{-2} + 31Fe^{+2} + 62Fe^{+3} + 40CaCO_3 \rightarrow 31Fe_3O_4 + 40Ca^{+2} + 20C + 20CO_2\,, \\ (2441.20\ \text{Å}^3)\ \ (2275.40\ \text{Å}^3)\qquad (179.40\ \text{Å}^3) \end{array}\right\} \quad (37)$$

Volume difference = 0.55 per cent ;

$$\left.\begin{array}{c} 28O^{-2} + 10Fe^{+2} + 20Fe^{+3} + 12CaCO_3 \rightarrow 10Fe_3O_4 + 12Ca^{+2} + 12CO_2\,, \\ (732.36\ \text{Å}^3)\ \ (734.00\ \text{Å}^3) \end{array}\right\} \quad (38)$$

Volume difference = 0.22 per cent.

The main difference between equations (37) and (38) lies in the presence of graphite in the solid product of the former and its absence in that of the latter. In general it can be said that a comparative abundance of oxygen ion in the ore-forming fluid would favor the reaction of equation (37) and a deficiency in that ion, that of equation (38).

Two equations, analogous to (35) and (36), can be written for the replacement of calcite by zincite, as follows:

$$4Zn^{+2} + 2CaCO_3 \rightarrow 4ZnO + 2Ca^{+2} + C + CO_2\,, \quad (39)$$

$$Zn^{+2} + CaCO_3 \rightarrow ZnO + Ca^{+2} + CO_2\,. \quad (40)$$

These can be modified in the same manner as equations (35) and (36):

$$\left.\begin{array}{c} 19Zn^{+2} + 8CaCO_3 + 3O^{-2} \rightarrow 19ZnO + 8Ca^{+2} + 4C + 4CO_2\,, \\ (488.24\ \text{Å}^3)\qquad (447.64\ \text{Å}^3)\qquad (35.88\ \text{Å}^3) \end{array}\right\} \quad (41)$$

Volume difference = 0.97 per cent ;

$$\left.\begin{array}{c} 13Zn^{+2} + 5CaCO_3 + 8O^{-2} \rightarrow 13ZnO + 5CO_2 + 5Ca^{+2}\,, \\ (305.15\ \text{Å}^3)\qquad (306.28\ \text{Å}^3) \end{array}\right\} \quad (42)$$

Volume difference = 0.37 per cent.

Again the main difference between these last two equations, as was true of equations (37) and (38), is in the presence of graphite in the solid product of the one and its absence in the other. Both reactions require the addition of oxygen from the solutions; if the amount available is small, the formation of graphite will be favored. Reactions such as those of equations (37) and (41) may explain why graphite is found in pyrometasomatic deposits in pre-Cambrian limestones, such as that at Franklin, New Jersey.

Because of the relatively large proportion of oxygen in the calcite molecule, there would be an excess of oxygen in most ore oxide–calcite replacements, were it not for the necessity of removing some or all of the carbon of the calcite from the system. It is the need for oxygen to combine with the excess carbon, joined to the requirements of the ore oxide molecule, that forces the addition of oxygen from the ore fluids. As a result of this situation, oxygen (as free oxygen or oxygen ion) could be

given up to the solutions only if the replacing ore oxide required so little oxygen as to leave enough to form CO_2 from all the carbon not changed to graphite and some to spare. If the oxygen so produced were to be converted into oxygen gas, the simultaneous reduction of some oxidizing agent, such as ferric ion, would be necessary.

CONCLUSIONS

The discussion presented in this paper indicates that it is possible to write equations for both supergene and hypogene replacement reactions which are balanced molecularly, volumetrically, and electrically. Complete equations for the average supergene metasomatism have been written which are probably close approximations of the truth. On the other hand, equations for hypogene reactions, in most cases, have been written only in skeleton form, though they are balanced in all respects.

To write the equation for a supergene replacement, the first step is to write the simplest molecularly balanced equation possible. This equation will be found to fit one of three general types. The first of these, type 1, shows that the volume of the replacing mineral provided is greater than the volume of the host. There must, therefore, be some additional amounts of the replaced mineral included on the left side of the equation and converted to soluble products on the right. This change is essentially one of oxidizing the sulfide ion to the sexivalent sulfur of the sulfate anion. This requires a strong oxidizing agent, and it is thought that the reduction of ferric to ferrous iron should be capable of doing the task. The second of these, type 2, shows that the volume of the replacing mineral produced by the reaction is less than that of the mineral replaced. It follows that more of the replacing mineral, both anion and cation, must be transferred from the liquid to the solid phase. Because the solubility of most sulfides, except hydrogen sulfide, in supergene solutions probably is negligible, the extra S^{-2} needed must come from H_2S or from the reduction of the sexivalent sulfur of the sulfate radical to the sulfide ion. This latter suggestion requires a strong reducing agent, and it is suggested that the oxidation of certain rather uncommon ions, such as Cd^{+1}, Mo^{+3}, etc., may drive the reaction forward. The third and last of these equations, type 3, indicates a volume of guest equal to that of host. Reactions for which equations of this type can be written appear to be exceedingly rare.

In this paper the main reliance, for both oxidation of S^{-} and reduction of S^{+6}, has been placed on half-reactions which undoubtedly occur in nature but which are not experimentally shown to do the work required of them in the volumetrically balanced equations here presented. It is pointed out that the oxidation of S^{-2} and the reduction of S^{+6} cannot take place in any area of chemical continuity at one and the same time.

The writing of equations for hypogene metasomatic reactions is far more difficult than expressing those which occur under supergene conditions. Too little is known of the composition and chemical nature of the ore-forming fluid to permit more than a skeleton presentation of the obvious essentials of the reaction. Again, however, three general types of equations can be set up. Type 1 includes those in which the amount of sulfur available in the host is greater than that needed to produce an equivalent volume of guest. This unwanted sulfur is removed by its oxidation to sexivalent positive sulfur of the sulfate ion. For this task the reduction of ferric to ferrous

ion is considered adequate. Type 2 contains those reactions in which the amount of sulfur available in the host is less than that required in an equal volume of guest mineral. This additional sulfur is here considered to be supplied directly from the ore-forming solutions as sulfide ions. No opinion is expressed as to how these sulfide ions are made available by the solutions in question. It is possible that some of this sulfur may be produced by the reduction of sulfate ion, but it is believed that the evidence at hand is against a wide application of this method. Finally, in type 3 are placed those reactions in which sulfur in the host is exactly equal to that required by an equal volume of guest. Such reactions appear to be quite uncommon.

In hypogene reactions involving the replacement of carbonates and silicates by sulfides, fluorides, and oxides, three types of reactions also are recognized. If there is no common ion in such reactions, the problem of writing a balanced equation is a matter of equating volumes alone. This is true of replacements of oxides and silicates by minerals with sulfide or fluoride anions (or any of the many other anions not considered here). If both guest and host contain oxygen ions, however, the three possible types of reaction are similar to those just discussed for hypogene sulfide replacements. In all the equations of this type, oxygen is present in the calcite in amounts over and above the requirements of the ore oxide but is never in sufficient abundance to satisfy, as well, the needs of silicon or carbon which had to be converted to silica or carbon dioxide. Only in rare instances would the oxygen needed by the ore oxide be so low as to allow the release of oxygen as such to the solutions. If oxygen is deficient, it is shown as being added directly from the solutions as oxygen ions, and no attempt is made to explain its presence there in that form. No equations of the third, or originally balanced, type are given.

Finally, it must be remarked again that this paper is designed to show, not what reactions take place during hypogene and supergene replacements, but rather that equations for such reactions can be written and that they can be balanced molecularly, volumetrically, and electrically, once the data are available with which to write them. Those equations which have been presented are not the only possible ones that could have been written for the reactions with which they deal. They are, however, possible and in many cases even probable explanations of what occurs during replacement reactions. If these equations do nothing more, they demonstrate the truth of Emmons' remark (1940, p. 159) that replacement is definitely not a molecule-for-molecule exchange. It is much more than that, but that, too, is amenable to exact chemical expression.

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REVIEWS

"Die Metamorphose der Kohle und ihr Einfluss auf die sichtbaren derselben." By W. PETRASCHECK. (*Akad. Wiss., Math.-naturwiss. Kl., Sitzungsber. der österr.*, vol. 156, pt. 1, nos. 7 and 8.) Pp. 375–444.

This article is a study of coal metamorphism based partly on the published opinions of numerous individuals, on the author's extensive knowledge of European low-rank coals and coal beds, and on the results of experimentation with the autoclave, using wood and coals of various ranks, but mainly soft brown coal, in reproducing the effects of coalification artificially. This latter work was incidental to studies in the production of binderless briquets from lignite (soft brown coal). To those interested in the geological phenomena of coal metamorphism as an approach to the geochemical study of coal constitution this article will be of special interest.

At the start the author differentiates the process of coal formation from peat from the process of coal metamorphism. The first process is described as a biochemical process and receives little attention. The metamorphic process is a geological process and forms the main subject of consideration.

Metamorphism of coal is of two varieties—thermal and kinetic (p. 377), with differences often difficult to distinguish except immediately adjacent to igneous contacts. Metamorphism results in the so-called "coal series" of rank variation. In the low-rank coals (brown coal) Petrascheck lists the ranks of coal based upon differences in moisture content (p. 382) as shown in the accompanying tabulation.

Coal Type	Per Cent Moisture
Earthy brown coal	40–60
Soft brown coal	30–40
Matt-brown coal	20–30
Bright-brown coal	8–16

(American classification probably would draw the line between subbituminous coal and lignite at about 30 per cent moisture; the boundary between subbituminous coal and high volatile carbon bituminous coal possibly lies between matt-brown coal and bright-brown coal, but American differentiation is made on a B.t.u. basis, not on a moisture-content basis, so there is probably some overlapping.—G. H. C.)

What is called a "Schürmann's law" (p. 382) covers the relationship of moisture content to depth of cover for these low-rank coals and calls for a decrease of 1 per cent moisture for each additional 100 feet of cover, being based upon observations in East Borneo. Ordinarily low-rank coals do not have a depth of cover adequate to test the validity of the law.

Discontinuity of the coal metamorphic series is suggested (p. 383). (It may be indicated by the break in the moisture content between the matt-brown coal and the bright-brown coal as indicated in the table above. The author does not mention the work of Seyler in England, who claims discontinuity through the entire coal series on the basis of reflectivity studies.—G. H. C.) Petrascheck reserves opinion as to the discontinuity of the coal series in general.

Attention is called to the parallel consolidation effect of metamorphism upon coal bed and associated rocks, particularly clays and sandstones. Coal was pointed out by David White (p. 380) as a scale for measuring the milder stages of metamorphism.

The differentiation of peat and brown coal has been based upon the somewhat questionable distinction that moisture can be squeezed out of peat but not out of brown coal. Petrascheck cites evidence that it has been forced out of soft brown coal.

In general, it is the author's thesis (p. 388) that temperature above 100° C. enters very little into coal metamorphism except in thermal alteration. Static pressure is important up to a point, but tangential (kinetic) pressure is much more important. The unimportance of temperature is indicated particularly by the fact that resins, which melt at a relatively low temperature (less than 250° C.) have not been affected by metamorphism unless the coal has suffered thermal alteration.

The banded ingredients (vitrain, durain, etc.) are believed to exercise no influence upon coal rank.

The autoclave investigations (pp. 389–404)

were carried on with small cubes of material cut from coal still containing the bed moisture. A pressure of 48–50 atm. was maintained in the autoclave, and a differential pressure, usually of 1 kg/cm,² was applied to the coal by weights at a temperature of 250° C. for 2 hours. The autoclave was always filled with water. Most tests were made with Köflach (Styria) soft brown coal. The coal was maintained in a moist condition to avoid changes inevitable if it was allowed to air-dry.

Volume and weight losses always appeared (p. 393). Some cubes were also deformed by unequal dimensional shrinkage. By these tests Petrascheck believed he demonstrated that metamorphism resulted in the destruction of cellulose, that lignified tissue produced vitrain, that fusain-like material was produced from green or dry wood, and that moor peat produced durain. Woods that have suffered much decay and have lost their cellulose before incoalation are much compressed.

That the autoclave tests were simply a mild form of low-temperature carbonization, as claimed by some (p. 395), Petrascheck denies, because there was not the characteristic production of tars and low-temperature gases, because there is selective disappearance of cellulose and the formation of a vitrain-like material from the wood, and because the pitchlike material that resulted resembled vitrain rather than tar, since it possessed typical wood structure in thin sections. Cell shrinkage corresponded to that observed in naturally formed coals.

In discussing the changes that take place in the structural components of coal (pp. 404–422), Petrascheck considers wood, fusain, durain, and the resins. The effect of metamorphism on wood is regarded as varied, depending upon whether cellulose had been lost through bacterial action before incoalation or later by metamorphism. In the first case the material is readily compressed with the loss of cell structure; in the latter case the presence of cellulose in the early stages of metamorphism tends to protect the cell structure, and the vitrain bands resulting from coalification are likely to preserve the cell structure, although the material consists largely of coalified lignin. (Undoubtedly, the claim that cellulose is lost through the metamorphic process will cause some lifting of the eyebrows on the part of botanists interested in the study of coal as a fossil material. Apparently, Petrascheck [p. 405] regards the good preservation of wood structure in vitrain bands as somewhat unusual. In Illinois coal beds the presence of such vitrain bands is of common occurrence, and bands have been seen as thick as 2–3 inches or more. The question may be raised whether the distinction between cellulose and lignin is sufficiently precise so that the layman can be sure that there is general agreement among botanists concerning the meaning of the terms.—G. H. C.) Petrascheck calls attention to the fact that, under the particular P/T conditions applied, cellulose disappears in the autoclave. It also disappears, he says, between matt and glance brown-coal stages of metamorphism (p. 406). (Presumably that means that fossilized cell structures representing cellulose are not present in coals of bituminous and higher ranks, a conclusion that the American coal paleobotanist will probably not readily accept without substantial proof.—G. H. C.)

Fusain is discussed at length (pp. 408–415) and, although the objections to the forest-fire explanation are admitted—viz., the presence of resin in fusain, the rank of fusain, and the manner of occurrence of fusain—he concludes that the forest fire is the most probable mode of origin of most fusain. He has definite reservations in regard to the possible importance of hydrogen-ion concentration in the associated strata.

Petrascheck believes that evidence of "burned layers" is more common than has generally been conceded and that their absence in some coal beds is due to the fact that such beds were "low-moor" deposits periodically overwhelmed by water. Many other beds not so situated do contain "charcoal" layers.

The Mackenzie-Taylor theory of base exchange is interesting but inadequately proved. The author admits, however, that kaolinized bed partings in coal beds are commonly associated with abundant fusain, whereas fusain is not common in beds in which montmorillinite forms the chief mineral in clay partings.

The idea that fusain has a more or less fixed rank does not seem to be borne out by the evidence, according to Petrascheck. Using two charts (pp. 410, 412), in which volatile matter of fusain and of whole coal or of vitrain is plotted against rank, he shows that the variations in the fusain roughly parallel those in the whole coal or vitrain from the same beds, volatile matter decreasing with the rank of the coal and fusain.

The occurrence of resins in fusain (p. 413) is not regarded as fatal to the forest-fire theory, mainly, it appears, because charcoal may yield

bituminous substances. Possibly the resin problem is dismissed too lightly.

Various other considerations in regard to fusain are raised and explained, such as the fusainization of the inner or outer portions of stems, as the case may be, and the presence of fusain in coal balls, indicating that it originated in the moor deposit. The conclusion is reached that the forest-fire explanation is preferred to any other that has been proposed.

Durain (p. 416) is regarded by Petrascheck as coalified moor coal. The humic material present is derived from leaf debris rather than from woody stems. It is generally but not always noncoking, since the "coking capacity" of coal resides mainly in vitrain. Volatile matter is somewhat higher in durain than in vitrain, with which it may be associated. The origin of the opaque matter in durain is said to be the humic acids, but the explanation is unsatisfactory (p. 417). (No reference is made to explanations of opaque matter that have been advanced by R. Thiessen from time to time.—G. H. C.) Durain is regarded as a quiet-water deposit by Petrascheck and the association of durain with sponge spicules, diatoms, and other aquatic forms is cited as evidence. (The durain of Petrascheck is evidently both the clarain and the durain of British and American writers, as well as the opaque and translucent attritus of Thiessen. There is less discrimination with respect to the varieties of "durain" than seems to be employed by coal petrographers in this country.—G. H. C.)

Resins (pp. 418–422) of two kinds are recognized: resins representing plant secretions, called "retinite" or "resinite," and resins which are designated as "exudations." This latter material fills cracks and lies along bedding planes and apparently includes the so-called "organic minerals" known as duxite, hartite, and köflachite. It is relatively rare, and whether or not such material is found in American coals is not known by the reviewer.

Pollen, spores, cuticles, and waxy material provide the source of what Petrascheck calls the "polymer bitumens." The spores have important uses in stratigraphic geology. In general, spores and pollen in low-rank coals have the chemical characteristics of modern pollen. They provide a means of checking the temperature to which coals have been subjected, since they melt at less than 200° C. and decompose at temperatures between 300° and 350° C. In general, these substances disappear in the high-rank coals.

Finally, there is the material called "bituminous wood" by Petrascheck (p. 424), being a coal of a special light yellow color, displaying cellular structure, the megascopic appearance of vitrain, but very "bituminous." It is believed by the author of the paper to have originated from decayed wood.

One section of the article is given to the consideration of the effect of the hydrogen-ion concentration in the coal beds and in associated strata. High moors and forest peats are said to have an acid environment; low moors a neutral or weakly acid environment. Kaolin forms in an acid medium and montmorillinite in an alkaline medium. In general, as has been previously noted, fusain seems to be more abundant in coal beds containing kaolinitic clays than in those in which the clay is largely montmorillinite. (The extent to which these generalizations may apply to American coals is not known.—G. H. C.)

The latter part of the paper (pp. 429–439) concerns the tectonic evidences of metamorphism. These consist mainly in the development of joints. There is general increase in the amount of jointing with the degree of metamorphism, and jointing is more characteristic of tectonic than of thermal metamorphism. Optical changes (pp. 431–432) accompany alteration, the low-rank coals being isotropic and the higher-rank anisotropic. The boundary lies between the matt-brown coal and the glance or bright-brown coal. The extinction tends to be parallel to the bedding of a coal bed when the latter is horizontal or vertical; otherwise it is inclined to the bedding.

Special studies were made of the coals near Handlova, Czechoslovakia, Pernik, Bulgaria, and Salgotarjan, Hungary, to determine the relative importance of tectonic and thermal metamorphism. The discussion has local significance only.

The metamorphism of Sudetenland, Germany, brown coal (pp. 432–439) is also discussed, tectonic versus thermal metamorphism also being at issue. Jurasky has spoken for thermal metamorphism from a deep-lying magmatic center. Petrascheck, speaking for tectonic metamorphism, believes that gas bubbles in the resin, bitumen exudations (duxite), and a peculiar type of columnar cleavage in the coal, all of which are cited by Jurasky as evidences of thermal alteration, are found in coal beds that have been permanently cool. Other evidence is

cited for doubting even the existence of the deep-seated igneous center.

Toward the end of the article (p. 439) the author calls attention to the possible usefulness of kaolin and bentonite as geological thermometers. The first loses moisture at 450° C., and bentonite at 250° C. The evidence supplied by these minerals indicates that the Sudetenland coals did not reach the high temperatures suggested by Jurasky.

In summarizing the summary (pp. 439–442) note may be made of the following conclusions. Absolute differentiation of thermal and kinetic metamorphism is impossible. Volatile-matter content is not a suitable basis for the classification of brown coal; moisture content is satisfactory. Depth of overburden is not adequate as a sole cause of rank advance. Wood (vitrain) is the most reactive substance in coal, but cellulose is lost in the coalification process. Rotten and cellulose-free wood compresses very flat but possesses the megascopic appearance of vitrain. Moor coal is the source of durain. Autoclave tests substantiated the loss of cellulose under pressure. Fusain is generally derived from wood charcoal. Undulatory extinction is an attribute of resins of high-rank coal. The exudation of resin does not necessarily require thermal metamorphism. The degree of jointing and its character are a measure of the tectonic stress, as is likewise anisotropism beginning with bright-brown coal.

The article is well documented with 111 references mainly to German and Austrian literature but with a few English and American citations. Unfortunately, the references are not always adequately described so that they can be easily found.

G. H. Cady